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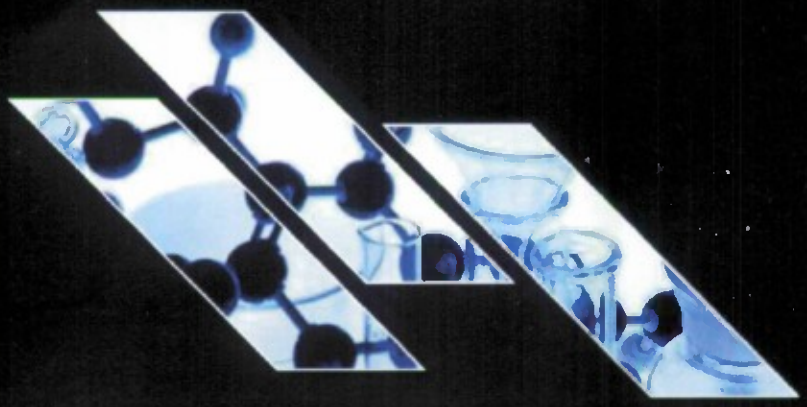
DIAL-A-DECON SOLUTION CHEMISTRY GAP TESTING



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The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorizing documents.

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14. ABSTRACT:
The Dial-A-Decon solution chemistry gap testing, documented in this report, was performed to fill some of the higher priority data gaps identified by the "Solution Chemistries for Point-of-Use Decontamination Formulation" report published by Noblis, Inc. (Falls Church, VA) in April 2009 for the Defense Threat Reduction Agency. The Noblis report included an assessment of the science that could be used in point-of-use formulation of decontaminants effective against the chemical warfare agents, sulfur mustard (HD), VX, and G agents, and the endospore biological agent, *Bacillus anthracis*. As part of their task, Noblis identified and prioritized data gaps from the available literature. The data gaps tested and reported here include the influence of solution pH on the reaction rate of VX with peracetic acid, peroxoborate, peracetylborate, peroxomonocarbonate, and percarbonate; the effect of solvent polarity on the reaction rate for VX and GD in solutions of peroxoborate, peracetic acid, and peroxomonosulfate; the influence of surfactant type on spore removal; the relationship between the surfactant hydrophilic lipophilic balance number and its ability to emulsify HD; and emulsion experiments to determine the concentration of HD, emulsified as a function of the surfactant concentration.

15. SUBJECT TERMS

Point-of-Use	Peracetic acid	Peroxoborate	Peracetylborate
Peroxomonocarbonate	Percarbonate	pH dependence	HD emulsification
Reaction rate	Solvent polarity	Surfactant	Spore removal

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PREFACE

The work described in this report was authorized under Defense Threat Reduction Agency Joint Science and Technology Office (DTRA JSTO) project no. BA09PHM052. The work was started in January 2009 and completed in January 2010.

This report was published through the Technical Releases Office; however, it was edited and prepared by the Decontamination Sciences Branch, Research and Technology Directorate, U.S. Army Edgewood Chemical Biological Center (ECBC).

The use of either trade or manufacturers' names in this report does not constitute an official endorsement of any commercial products. Manufacturer names and model numbers are provided for completeness. This technical report may not be cited for purposes of advertisement.

This report has been approved for public release.

Acknowledgments

A program cannot be successfully completed without the contributions of a good team of people. The authors thank the following individuals for their hard work and assistance with the execution of this technical program:

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DIAL-A-DECON SOLUTION CHEMISTRY GAP TESTING

1. BACKGROUND

The Defense Threat Reduction Agency (DTRA) previously tasked Noblis, Inc. (Falls Church, VA) to perform an assessment of the science that could be used in point-of-use formulation of decontaminants effective against the chemical warfare agents sulfur mustard, VX, and G agents, and against the endospore biological agent, *Bacillus anthracis*. As part of the task, Noblis identified and prioritized data gaps in the available literature. The list of data gaps was published in April 2009 in their "Solution Chemistries for Point-of-Use Decontamination Formulation" report,[1] and summarized as follows:

Higher priority data gaps:

- The effects of surfactants and cosolvents on the rate of dissolution of sulfur mustard.
- The effect of surfactants on the peroxide-sulfide reaction.
- The pH dependencies of peroxomonocarbonate reactions with G agents and VX, the peroxoborate reaction with VX, and the peracetic acid reaction with VX.
- The effects of surfactants on the sporicidal efficacy of several biological decontamination solutions.

Medium priority data gaps:

- Solvent effects on peroxoborate reactions with HD, G agents, and VX; peroxomonosulfate reactions with G agents and VX; and peracetic acid reactions with HD, G agents, and VX.
- Effects of surfactants on peroxomonocarbonate reactions with G agents and VX; peroxoborate reactions with HD, G agents, and VX; and peroxomonosulfate reactions with G agents and VX.
- The optimum concentration of tetra-amido macrocyclic ligand (TAML) activator in sporicides.
- Effect of decontamination solutions at concentrations typically used for chemical decontamination on biological agents (which are typically higher than those studied for biological decontamination).

The Dial-A-Decon solution chemistry gap testing, documented in this report, was performed to fill some of these priority data gaps. The data gaps tested and reported here include the influence of solution pH on the reaction rate of VX with peracetic acid, peroxoborate, peracetylborate, peroxomonocarbonate, and perearbonate; the effect of solvent polarity on the reaction rate VX and GD in solutions of peroxoborate, peracetic acid, and peroxomonosulfate (Oxone); the influence of surfactant type on spore removal; the relationship between the surfactant Hydrophilic Lipophilic Balance (HLB) number and its ability to emulsify HD; and emulsion

experiments to determine the concentration of HD emulsified as a function of the surfactant concentration.

2. TEST MATERIALS, PROCEDURES, AND EQUIPMENT

2.1 Test Materials

The following materials were purchased from Sigma-Aldrich (St. Louis, MO): sodium percarbonate, sodium perborate monohydrate, sodium perborate tetrahydrate, peracetic acid 32 wt % in dilute acetic acid, sodium hydrogencarbonate, sodium phosphate monobasic, sodium phosphate dibasic dihydrate, sodium hydroxide, 1,2-propanediol, Span 80, Span 85, Tween 20, Tween 80, cetyl trimethyl ammonium bromide, sodium dodecyl sulfate, sodium sulfite, 2-propanol, acetonitrile, chloroform, and pH 11 and 12 hydrion buffer salts. Tergitol 15-S-3 and Tergitol 15-S-40 were provided by Dow Chemical Company (Midland, MI). P eracetyl borate (PAB, supplied as sodium borate peracetate, PES-Solid) was manufactured by Solvay Chemical GmbH (Rheinberg, Germany), and was provided by the Naval Surface Warfare Center Dahlgren Division. The pH 7 and 10 buffer solutions for pH electrode standardization were purchased from Fisher Scientific (Pittsburgh, PA). All chemicals were used without further purification. Water was purified using a GE Osmonics, Model E4-11000-DLX reverse osmosis water purification system.

The chemical agents used for these studies were Chemical Agent Standard Reference Material (CASARM) or CASARM high purity (HP) grade with purities on record obtained from either Nuclear Magnetic Resonance (NMR) or Gas Chromatograph/Mass Spectrometer (GS/MS) analyses. The chemical agents were obtained from the Chemical Transfer Facility (CTF). All purity documentation will be maintained by U.S. Army Edgewood Chemical Biological Center–Research and Testing (ECBC-R&T) to include lot number and manufacturer/supplier. The materials used in this test program, including lot, purity, and source are provided in Table 1. Chemical agents are used only in properly certified surety facilities, capable of handling such materials safely. Personnel handling the chemical agents have been fully trained and certified for such operations.

Table 1. Chemical agents used.

Contaminant	Grade	Lot	Density (g/mL)	Purity (%)
VX	CASARM HP	VX-U-7011-CTF-N	1.0083	89.5
GD	CASARM	GD-U-2323-CTF-N	1.0222	98.8
HD	CASARM	HD-U-5038-CTF-N	1.2680	98.4

2.2 Rate Measurements

Reactions were carried out in buffered water media. Phosphate buffer systems that would not interfere with the reactant species concentrations were selected; i.e., no carbonate or borate buffers were used. Background hydrolysis rates, as a function of pH, were determined by conducting identical studies using solutions without the active component. Studies were performed using three replicates. The oxidant concentration was 20-fold higher than that of the agent to maintain pseudo-first-order reaction conditions. Reactions were performed with pH values up to pH 11 or 12; however, because some reactions at higher pH did not follow linear first-order reaction conditions and

the replicates were inconsistent, the fidelity of the data to determine the observed reaction rates was uncertain and has not been presented in this report.

The buffer concentration was maintained at 0.5 M using sodium phosphate monobasic/dibasic or sodium phosphate dibasic/sodium hydroxide media. The solvent polarity studies containing propylene glycol used buffers at 0.1 M due to the diminished capacity of these systems to solvate buffer salts. Solutions were prepared in volumes of 60 mL to facilitate the accurate weighing of reagents and measurement of pH prior to testing. Solution pH measurements were taken using a VWR sympHony combination electrode, standardized using certified pH 7, 10, 11, and 12 buffer solutions as appropriate, interfaced with a Fisher Accumet model 25 pH meter, part number 300035.1. Due to the time required to make minor pH and volume adjustments, solutions were pre-equilibrated at the selected pH for approximately 5 min prior to the addition of the agent, with the exception of peroxomonocarbonate solutions.

Reactions were performed at 21 °C in water-jacketed mini-reactors. Reactions were initiated by the addition of agent to 10 mL of the pH-buffered oxidant solution. Solutions were magnetically stirred on a multiposition magnetic stir plate, with the resulting vortex reaching approximately ¾ down into the solution. Sample aliquots of 0.35 mL were removed from the reaction mixture at specified time intervals and added to extraction vials containing 2 mL of a 0.2M sodium sulfite quench solution and 10 mL of chloroform. The quench solution for VX also contained 0.2M sodium carbonate to free-base any protonated VX that may have formed. Extraction vials were shaken vigorously for 10 s to partition the unreacted agent from the aqueous phase to the chloroform phase. Sample aliquots were removed from the chloroform phase and diluted in either 2-propanol, acetonitrile or chloroform prior to quantitation by LC/MS/MS or GC/MS.

Chloroform was used as the extraction solvent due to its ability to extract the chemical agent analytes of interest from aqueous solutions, while separating from the water in a distinct layer. This layering of chloroform and water made it possible to aliquot an analytical sample from the reaction solution.

All dilutions were prepared using Gilson Microman positive-displacement pipettes (Gilson product numbers M10, M25, M100, M250, M1000). The pipette size used was determined by the amount of extraction solution to be delivered. The analytical GC vials used were certified, 2 mL-wide opening, screw-top glass vials (Agilent).

The extraction samples generated were analyzed on a chromatograph, refer to Section 2.9 Sample Analysis for more information.

2.3 Surfactant Effect on Spore Removal

2.3.1 Panel Materials

The three military relevant materials, glass, butyl rubber, glass, and chemical agent resistant coating (CARC)-painted steel were procured from high volume retail sources (Table 2-2). Panels were cut to 2 x 5 cm size by the Advanced Design and Manufacturing Team, Engineering Directorate, at ECBC, APG. Table 2 summarizes the material source information.

Table 2. Panel materials.

Material	Vendor	Catalog
Glass	McMaster Carr	8481K74
Steel	Durrett Sheppard	11 Gauge A572, Grade 50, sheet 4'x8'
CARC paint	Automated Coatings	Primed and painted per MIL-C-53039A, 383 Green
Butyl rubber, 1/8 in. thick	McMaster Carr	8609K35

2.3.2 Spore Inoculation and Recovery

The bacterial strain used for these studies was plasmid-free avirulent *Bacillus anthracis* ΔSterne. Panels were inoculated with 5 x 10 µL drops of the spore stock containing 2 x 10^8 colony forming units (cfu)/mL and allowed to dry overnight in BioSafety Cabinet. The next day, inoculated panels were aseptically transferred to 50 mL sterile Falcon recovery tubes containing 20 mL of a 0.01% test surfactant solution.

The standard protocol for recovery of *Bacillus anthracis* ΔSterne spores from panels uses buffered peptone water (BPW) with 0.05% Tween 80 surfactant in the recovery solution. To isolate the contribution of the test surfactant, the BPW was not used and only the test surfactant was present in the recovery solution. The test surfactant solutions were tested at 0.01% due to excessive foaming when 0.05% cetyl trimethyl ammonium bromide (CTAB) was vortexed. Spores were extracted from panels with vortex physical treatment. To isolate the effect of spore removal to the test surfactant solution in the presence of the vortexing procedure and to minimize variability, wipes and swabs were not used. The tubes containing the panels were pulse-vortexed using a high capacity pulse vortexer (Q Glass Co., NJ) for 2 min at a maximum speed of approximately 1500 rpm as outlined in the recovery protocol.[2]

The tubes were serially diluted using Butterfield's buffer solution and plated in triplicate on Tryptic Soy Agar. Plates were enumerated the following day and the recoveries were calculated, taking into account the dilution scheme. Dilutions that had 20 to 200 colonies per plate were counted. The average from the three plates (triplicate) was used and multiplied by the dilution factor to yield cfu/mL. Then all five counts (five panels per surfactant) were averaged for each surfactant to yield final recoveries.

2.4 Surfactant Effect on HD Emulsification

Experiments were conducted to investigate the emulsification of HD in the presence of surfactant solutions prepared with a range of HLB values. Surfactant solutions with HLB values ranging from 4 to 18 were introduced in water-jacketed, 20 mL glass reaction vessels maintained at 21° C. Studies were initiated by the addition of 200 µL HD to 10 mL of the surfactant solution. The energy to create the oil in water (O/W) emulsions was provided by magnetic stirring. Solutions were magnetically stirred on a nine-position stir plate (Corning, model 440826) using ⅜ in. Teflon-coated stirring stars (VWR, Spinplus®, cat. no. 58947-820), which provided good magnetic coupling and a stable deep vortex reaching approximately ¾ into the solution. The multiposition stirrer was used to provide a consistent input of energy to multiple test solutions simultaneously. The combination of energy input, and the presence of surfactants to lower the interfacial tension, produced O/W emulsions of HD. Following a 45 min stirring period, the stirring was stopped and the emulsion allowed to sit for 1 min to allow the non-emulsified HD to settle out. Sample aliquots of 0.35 mL were removed from the center of the emulsified HD solution and added to 20 mL extraction vials containing 10 mL chloroform and 2 mL of water. Extraction vials were shaken vigorously for 10 s to partition the HD into the chloroform phase for analysis. Sample aliquots from the chloroform phase were removed and diluted in chloroform for HD quantitation by GC/MS. The tests followed

the general procedure used in "Solubilization of Nonaqueous Phase Liquid Hydrocarbons in Micellar Solutions of Dodecyl Alcohol Ethoxylates" *Environ. Sci. Technol.* 1994, *28*, 1829-1837.

The HLB system is a useful tool for finding a suitable emulsifying system. To emulsify a mixture of water and oil such as HD, one or more emulsifiers are required. Each surfactant system can be characterized by an HLB value. This value depends on the nature of the oil and the product application. The application where water dominates and the oil forms droplets is designated as an O/W system. The HLB system predicts the optimum emulsion stability when the HLB value of the surfactant systems matches the required HLB of the O/W system. Therefore, the required HLB is the value at which enhanced emulsion stability can be attained.

The theoretical HLB value for a mixture of surfactants is given by eq (1):

$$HLB_{mixture} = x_1 HLB_1 + x_2 HLB_2 \quad (1)$$

where x_1, and x_2 are the weight fraction of the two surfactants with HLB_1 and HLB_2. Binary mixtures of non-ionic surfactants were prepared to yield a range of HLB values.

Tergitol surfactants, with a total contribution of 5 wt %, were blended as shown in Table 3 to yield solutions with desired HLB values.

Table 3. HLB of binary Tergitol surfactant blends.

HLB	Surfactant 1	Weight Fraction	Surfactant 2	Weight Fraction
8	---	0.00	Tergitol 15-S-3	1.00
10	Tergitol 15-S-40	0.20	Tergitol 15-S-3	0.80
12	Tergitol 15-S-40	0.40	Tergitol 15-S-3	0.60
14	Tergitol 15-S-40	0.60	Tergitol 15-S-3	0.40
15	Tergitol 15-S-40	0.70	Tergitol 15-S-3	0.30
16	Tergitol 15-S-40	0.80	Tergitol 15-S-3	0.20
17	Tergitol 15-S-40	0.90	Tergitol 15-S-3	0.10
18	Tergitol 15-S-40	1.00	---	0.00

Span/Tween surfactants were blended as shown in Table 4 to yield solutions with desired HLB.

Table 4. HLB of binary Span/Tween surfactant blends.

HLB	Surfactant 1	Weight Fraction	Surfactant 2	Weight Fraction
4	Span 80	0.88	Span 85	0.12
6	Span 80	0.83	Tween 80	0.17
8	Span 80	0.65	Tween 80	0.35
10	Span 80	0.46	Tween 80	0.54
12	Span 80	0.28	Tween 80	0.72
14	Span 80	0.09	Tween 80	0.91
16	Tween 20	0.66	Tween 80	0.34
16.7	Tween 20	1.00	---	0.00

2.5 Emulsification as a Function of Surfactant Concentration

Emulsification experiments were conducted to determine the concentration of HD emulsified as a function of the surfactant concentration. The solutions tested were prepared from a binary blend of 0.60 weight fraction Tergitol 15-S-3 and 0.40 weight fraction Tergitol 15-S-40 surfactants with a calculated theoretical HLB value of 12. Surfactant concentrations ranging from 0.5 to 10 wt % were tested using the same procedure used to determine emulsification. In addition to a one minute static period, a 4 h static period was also tested.

2.6 Surfactant Effect on GD and VX Reaction Rate

The surfactant effect on percarbonate reactions with VX and GD was studied. Reactions were performed in aqueous solutions containing 0%, 1% (0.27 M), 2% (0.55 M), and 5% (0.82 M) surfactant. VX and GD reactions were performed at pH 10 and 9, respectively. The kinetics of 0.005 M VX and GD neutralization by 0.1 M percarbonate was investigated in aqueous cationic micellar media at 21° C.

2.7 Solvent Polarity Effect on VX and GD Reaction Rates

The effect of solvent polarity on the observed reaction rate of agents VX and GD was studied in solutions of peroxoborate, peracetic acid, and peroxomonosulfate (Oxone). Polarity of the reaction media was varied using aqueous solutions containing 0, 10, 20, and 30% propylene glycol. Using the dielectric strength as a measure of solution polarity, the polarity of the reaction solutions was varied by mixing water and propylene glycol in various proportions by volume. Calculations of the dielectric constant of the mixture were based on eq (2).

$$E_{mixture} = F_{water} \bullet E_{water} + F_{propylene\ glycol} \bullet E_{propylene\ glycol} \quad (2)$$

where

F = volume fraction

E = dielectric constant

The dielectric constant values for the mixtures are shown in Table 5.

Table 5. Dielectric constant values for water/propylene glycol solutions.

Mixture Dielectric Constant	Water, Volume Fraction	Water Dielectric Constant	Propylene Glycol, Volume	Propylene Glycol Dielectric
80.1	1.0	80.1	0.0	32.0
75.3	0.9	80.1	0.1	32.0
70.5	0.8	80.1	0.2	32.0
65.7	0.7	80.1	0.3	32.0

As the solutions became less polar, they were less able to solvate salts. The lower range of the dielectric constant was limited by the ability of the water/propylene glycol solutions to completely solvate the buffer salts. Therefore, the volume fraction of propylene glycol in the solutions was limited to an upper value of 0.3, and the buffer strength was maintained at 0.1M to allow complete dissolution of the salts.

2.8 The Test Preparation

Before each test was started, preparation was done in accordance with the Source Document.[3] The materials used in the methods were traceable, controlled, and identified according to the test plan. Instrumentation and equipment were verified and calibrated on a routine basis. Laboratory tools, such as pipettes, were used in accordance with the vendor's instructions, and any applicable ISO standards. All information was recorded and reviewed for accuracy, in keeping with good laboratory practices.

The test personnel were trained and approved to work with chemical agents. Program personnel adhered to the security, health, and safety requirements of the U.S. Army Research, Development, and Engineering Command (RDECOM) including, but not limited to, good laboratory safety practices, using safety office approved methods, and wearing proper personal protective equipment (PPE).

2.8.1.1 Vial Traceability and Labeling

To ensure traceability of the extract, taken at any point in the test process, each test vial was labeled.

2.8.1.2 Staggered Timing Charts

Test planning included the timing of each step, which was delineated by a staggered timing chart. The time between tasks depended on the limiting steps of the method. Once a test was begun, event timing was crucial, and the span between events should have been minimized. Event times that were outside the acceptance criteria could have induced error and/or bias into the final test results. This had the potential to make the test results unusable, especially for regulatory requirement test-to-test and lab-to-lab comparisons.

2.8.1.3 Dose Confirmation

To reference the concentration of agent challenge, dose-confirmation samples were prepared, diluted, and analyzed tin a manner similar to that used in the experimental procedure.

The results of the dose-confirmation sample analysis were used to calculate the reduction in starting challenge. An average of the dose-confirmation samples was calculated. The

effectiveness of the decontaminant and how much the agent interacted with the panel material could be evaluated by obtaining the concentration of the dose, and comparing this to the samples obtained after decontamination.

Table 6 provides a summary of the extraction solvent evaluated in the testing.

Table 6. Extraction solvent used.

Solvent	CAS	Source	Grade	Purity	Lot
Chloroform	67-66-3	Sigma-Aldrich (Product # 414697)	Capillary GC grade, stabilized with amylenes	≥99.9%	002242ME

All dilutions were prepared using Gilson Microman positive displacement pipettes (Gilson product numbers M10, M25, M100, M250, M1000). The pipette size used was determined by the amount of extraction solution to be delivered. The analytical GC vials used were certified, 2 mL-wide opening, screw-top glass vials (Agilent).

The extraction samples and sorbent tube samples were analyzed on a chromatograph, refer to Section 2.9 Sample Analysis for more information.

2.9 Sample Analysis

Sample analysis is performed on state-of-the-art analytical instrumentation with detection capabilities selective and sensitive enough for separation and trace-level detection of analytes of interest from complex matrices. Separation of analytes is performed by either liquid chromatography (LC) or gas chromatography (GC), depending on the sample to be analyzed. Detection is performed by a mass spectrometer (MS) for confident quantification and identification of the analytes of interest. A list of the instrumentation used for the analysis of program samples, generated during decontamination testing, is found in Table 7.

Table 7. Analytical instrumentation.

Analytical Platform	Description	Typical Use
GC/MS	**System:** Agilent 6890/7890 Gas Chromatograph (GC) equipped with a 5975 Mass Selective Detector (MSD) **Sample Injection System:** Gerstel multipurpose automatic liquid sampler (MPS 2) and Gerstel Cooled Injection System (CIS4) inlet **Ionization:** Electron impact ionization (EI) and mass filtering in the selective ion monitoring (SIM) **Flow Switching:** Agilent Microfluidics Deans Switch **Detection:** MS in selective ion monitoring (SIM) mode of acquisition **Software:** Gerstel Maestro software and Agilent Technologies MSD ChemStation software package (v. E.02.00)	Liquid samples from contact, remaining agent and residual agent tests

Table 7. Analytical instrumentation (continued).

Analytical Platform	Description	Typical Use
LC/MS/MS	**System:** Agilent 1200/1290 series LC and Applied Biosystems API5000/5500 Triple-Quadrupole Mass Spectrometer equipped with a TurboV Ion Source **Sample Injection System:** Agilent Binary Pump and High Performance Automatic Liquid Sampler (ALS). **Ionization:** Electrospray ionization (ESI) **Ancillary Equipment:** Degasser, Thermal Column Compartment (TCC), and an ALS thermostat **Detection:** MS/MS; multiple-reaction monitoring (MRM) **Software:** Applied Biosystems Analyst software package (v. 1.4.2)	Liquid samples from contact, remaining agent and residual agent tests

2.9.1 Analytical Data Acquisition

Analytical data is acquired for each individual sample introduced to the instrument. For confident quantification and reporting of found concentrations from unknown samples, calibration of the analytical instrument, prior to sample analysis, is essential. Instrument calibration establishes a relationship between known concentrations of calibration standards and the detector response that is returned during analysis. This relationship is represented by a calibration curve where the detector response is plotted versus the known concentration. Found concentration is determined by comparing detector response from unknown samples back to the relationship, or model, established by calibration of the instrument.

Each analytical method requires calibration standards, prepared in high purity solvent at multiple concentration levels, to generate a calibration curve. All calibration standards are prepared volumetrically from neat agent of known density and purity. The starting material is acquired from the U.S. Army Edgewood Chemical Biological Center (ECBC), Agent Chemistry Branch. All purity documentation is maintained by ECBC-Research and Technology (R&T), to include lot number and manufacturer/supplier. Volumetric dilution is performed following a pre-determined serial dilution scheme. Post-preparation, calibration standards are aliquoted as sets of standards into autosampler vials.

A fresh set of calibration standards is analyzed for each analytical queue. After analysis, the calibration curve is established using the appropriate curve model and weighting. A calibration curve must yield the reported concentration percent recoveries (evaluated as Recovery-1) for each level at ±20%, compared to the expected concentration. If a calibration level does not meet this acceptance criterion, it is removed from the calibration curve and the curve is re-evaluated. No more than three calibration levels may be removed from within the analytical range. A minimum of seven calibration levels are required. If more than three levels are removed, if there are less than seven calibration levels, or if either the low or high calibration levels are removed, the Quality Manager is consulted and corrective action may be required. Corrective action may require re-calibration, preparing new calibration levels and/or re-analyzing all samples from the queue. The calibration also allows a limit of detection (LOD) and limit of quantification (LOQ) to be calculated. These values give confidence in the reported concentrations at the very low end of the calibration

range and characterize the detection and quantification abilities of the instrument for a particular sample queue.

Additional processes are in place to ensure confidence in the results obtained from analysis of samples on the analytical instrumentation. Along with the calibration standards, other quality samples such as blank and CCV samples are analyzed to ensure instrument control and continued confidence in the analytical results. After the calibration standard analysis is completed, solvent blanks and multiple concentrations of CCV standards are analyzed regularly, throughout a sequence of samples, to validate the instrument calibration. This ensures that the instrument remains in calibration control for continued confidence in the reported results of unknown samples. Furthermore, the regular analyses of CCVs enable trend analysis, determination of bias in sample analysis, detection of instrument drift and carryover, and provide information on the error in the reported analytical value. Typically, CCVs bracket 9–15 samples. If CCV-reported concentrations show a calculated percent recovery (evaluated as Recovery-1) greater than ±30%, corrective action is performed. Corrective action often results in a repeat analysis of samples. The repeat analysis, also referred to as re-runs, may consist of selected samples, or it may consist of re-analyzing the entire set of samples.

The analytical queue is also evaluated for sample performance. For confidence in the sample-reported concentrations, all values must fall within the analytical concentration range of the method. Samples with reported concentrations outside of this range require corrective action. Corrective action consists of repeating the analysis using new dilution factors for these samples to ensure response within the analytical range. Re-runs may be performed within the same queue by adding additional CCVs or may require a new queue with a new calibration evaluation. Re-runs are subject to the same queue setup and quality control requirements as the original samples. If a re-run is required for a particular sample, the analytical result from the re-run is used as the reported concentration in all follow-on data analysis.

2.9.2 Analytical Data Quality Review

After the analytical analysis is complete, all aspects of the process of acquiring the analytical data are reviewed and evaluated by the Quality Manager. The purpose of the analytical data quality review is to ensure confidence in the analytical data by verifying that the data acquisition was performed within established controls. If the analytical data quality review identifies any issues with the data that would question the confidence of the reported values, the discrepancies are recorded and corrective action is required. Corrective action may include, but is not limited to:

- Further investigation of individual chromatograms for sample chromatography peak performance, integration, etc.
- Additional re-runs and re-evaluation of data from reserve, or "Hold" test samples
- Instrument performance checks
- Visual verification of the sample to ensure there are no obvious reasons for sample analysis issues
- Repeat the experiment for select samples to re-generate samples for analysis

After the final analytical data quality review by the Quality Manager, the data evaluated will either be approved or rejected. Approved data may be used by the Primary

Investigator for the program that required the samples. Rejected data will be reported to the Branch Chief and may require repeat testing and/or further investigation.

3. RESULTS AND DISCUSSION

3.1 VX pH Dependence

3.1.1 Objective

When dissolved in aqueous media, many of the oxidants used for decontamination can exist in the neutral form and the conjugate base form, depending on the solution pH. These species exist in equilibrium with each other, and are highly dependent on the solution pH relative to the compounds dissociation constant, pK_a. Some oxidants dissolve to form multiple compounds, with associated complex equilibria determining the relative concentration of each species dependent on pH. The observed reaction rates are proportional to the concentration of these reactive species and their reaction profiles.

The objective of this study was to determine how the solution pH affects the reaction of VX with peracetic acid, peroxoborate, peracetylborate, peroxomonocarbonate, and percarbonate. This was accomplished through testing solutions of oxidant with VX and monitoring the reduction in VX concentration by chromatographic analysis of aliquot extracts. Concentrations of the active component were 20 times the agent concentration, thereby maintaining pseudo first-order reaction conditions throughout reaction period in the rates reported. The pH values were selected to bracket values below and above the pK_a of the oxidant to discern how these changes in pH relate to the observed rates.

3.1.2 Peracetic Acid

Under conditions with adequate buffer capacity and a 20-fold excess to VX, results from the testing of peracetic acid (also known as peroxyacetic acid) showed optimal VX neutralization at pH 9 as shown in Figure 1. With a pK_a value of 8.2, in solutions at pH 9 and above, most of the peracetic acid is in the anionic form and will provide enhanced reactivity over the non-dissociated form.[4]

The peracetic acid solutions prepared at elevated pH (pH 10-12) evolved gas, as evidenced by bubble formation, which was most likely oxygen resulting from the base, promoted by the decomposition of the peracetic acid and/or hydrogen peroxide. Peracetic acid decomposition may have contributed to the drop in reactivity seen at elevated pH. However, no attempts were made to determine the stability of peracetic acid in these alkaline solutions by measuring the oxidant concentration.[5] The background VX hydrolysis rates in solutions containing only the buffer component were very low relative to the neutralization rates provided by the peracetic acid solutions.

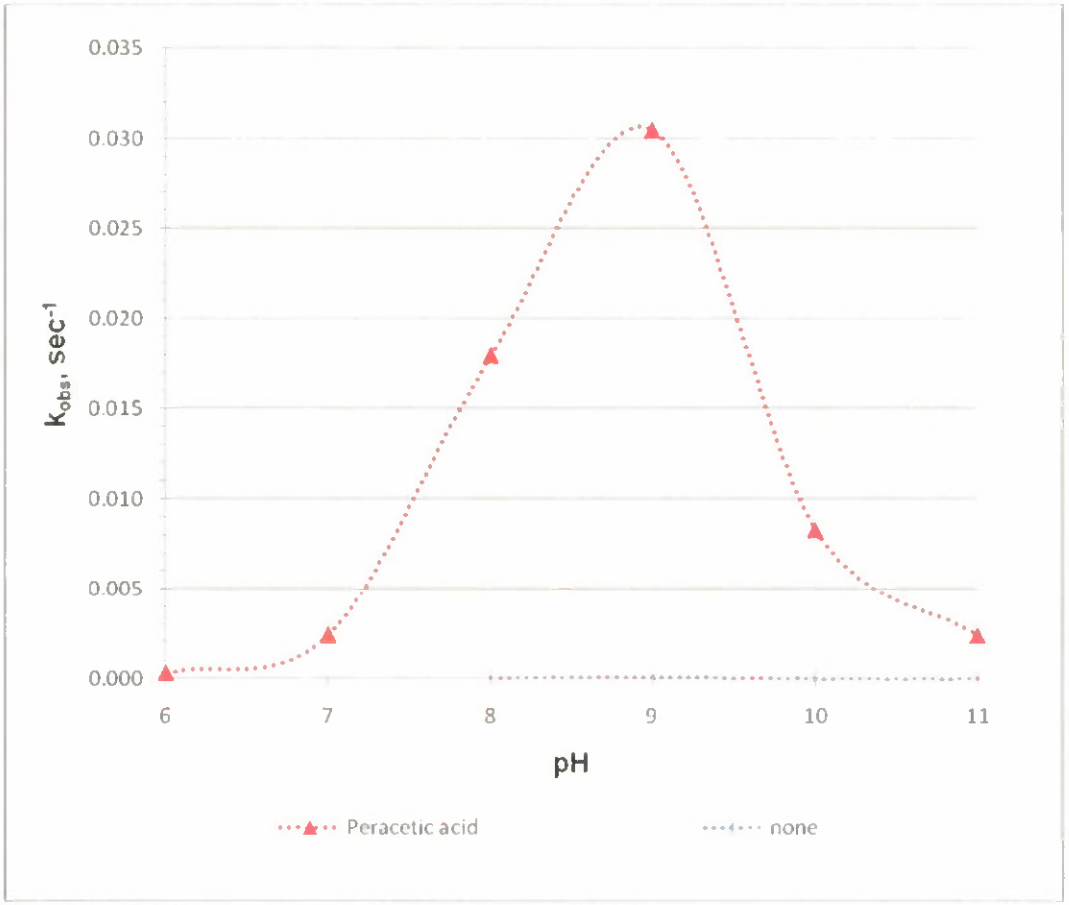


Figure 1. pH dependence of peracetic acid reaction with VX.

3.I.3 Peroxoborate

Peroxoborate solutions were prepared using sodium perborate. In the crystalline form, sodium perborate exists as a cyclic dimeric peroxodiborate anion with bridging peroxo groups and two four-coordinate boron atoms, $B_2(O_2)_2(OH_4)^{2-}$, which in aqueous media rapidly hydrolyze to form an equilibrium solution of hydrogen peroxide and tetrahydroxy borate anion, $B(OH)_4^-$ as shown in eq (3).[6-7]

(3)

The peroxoborate anion, $B(HO)_3(OOH)^-$, is formed by the equilibrium shown in eq (4). Peroxoborate functions as an active donor of hydroperoxide anion at lower pH than found with hydrogen peroxide alone, giving it an advantage in nucleophilic oxidations.[6] Peroxoborate is reported to be stable in solution.[8]

$$B(OH)_4^- + HO\text{-}OH \rightleftharpoons B(OH)_3 + H_2O + HOO^- \rightleftharpoons (OH)_3B(OOH)^- + H_2O \quad (4)$$

The observed reaction rate of VX in the peroxoborate solutions, shown in Figure 2, had a steady increase as the pH rose from 8 to 11, but markedly increased in the more alkaline pH 12 solution. At basic pH conditions, close to and greater than the pK_a (11.6) for hydrogen peroxide, the equilibrium for free hydrogen peroxide will shift to favor the hydroperoxide anion (HOO^-) and contribute to the reaction with VX via additional perhydrolysis, resulting from HOO^- substitution.[7, 9] This observed rate increase may be attributed to additional perhydrolysis contributions from the hydroperoxide anion produced at high pH.

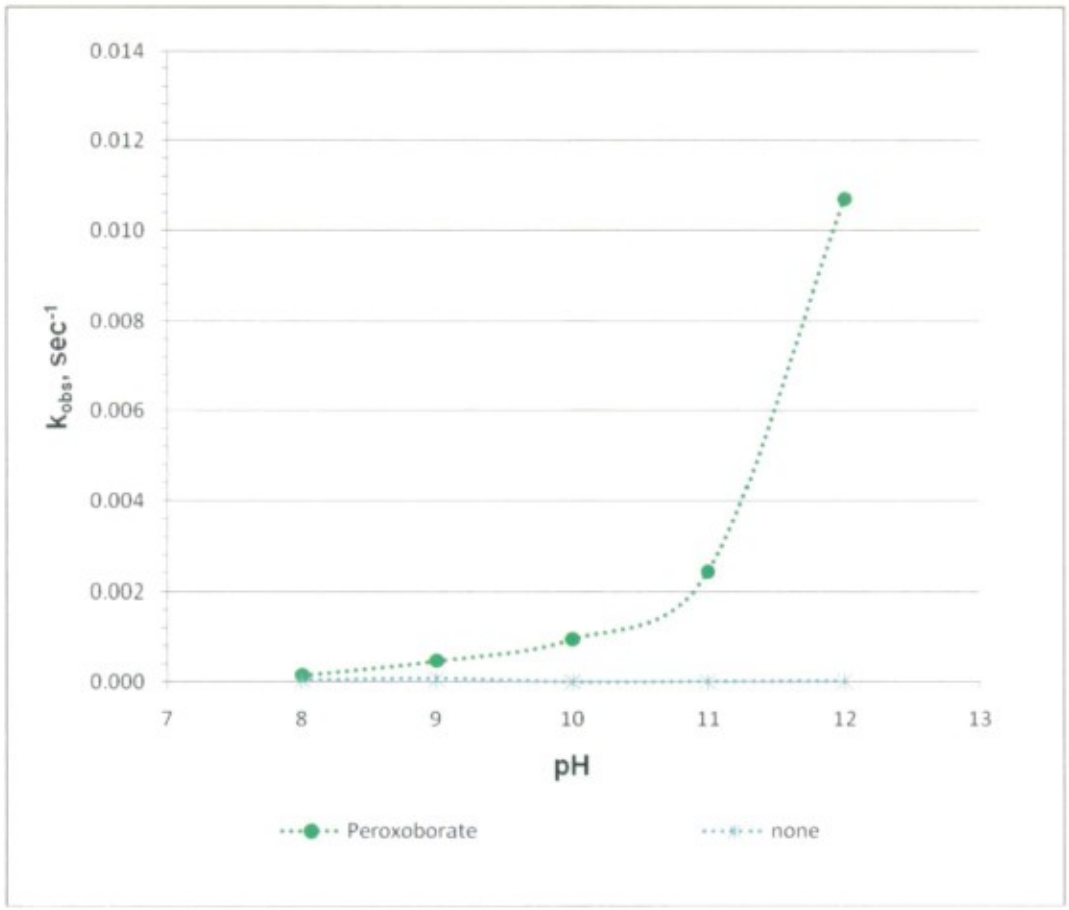


Figure 2. pH dependence of peroxoborate reaction with VX.

3.1.4 Peracetylborate

Peracetylborate is proposed to be a complex salt composed of a tetraborate core covalently linked with peracetic acid and acetic acid.[6] Peracetylborate is a source of peracetic acid when dissolved in water. Solvay Interox, a Belgian-based manufacturer of peroxygen compounds, has developed a patented, stable, solid form of a peracetic acid/borate complex (U.S. Patent No. 6,797,681). The U.S. Navy is collaborating with Solvay Interox to facilitate development of this technology.[10]

The observed reaction rate of VX in the peracetylborate solutions, shown in Figure 3, had an increase as the pH rose from 7 to 8. The reaction of VX with peracetylborate showed an optimal rate in solutions at pH 8. The observed reaction rate decreased slightly at pH 9.

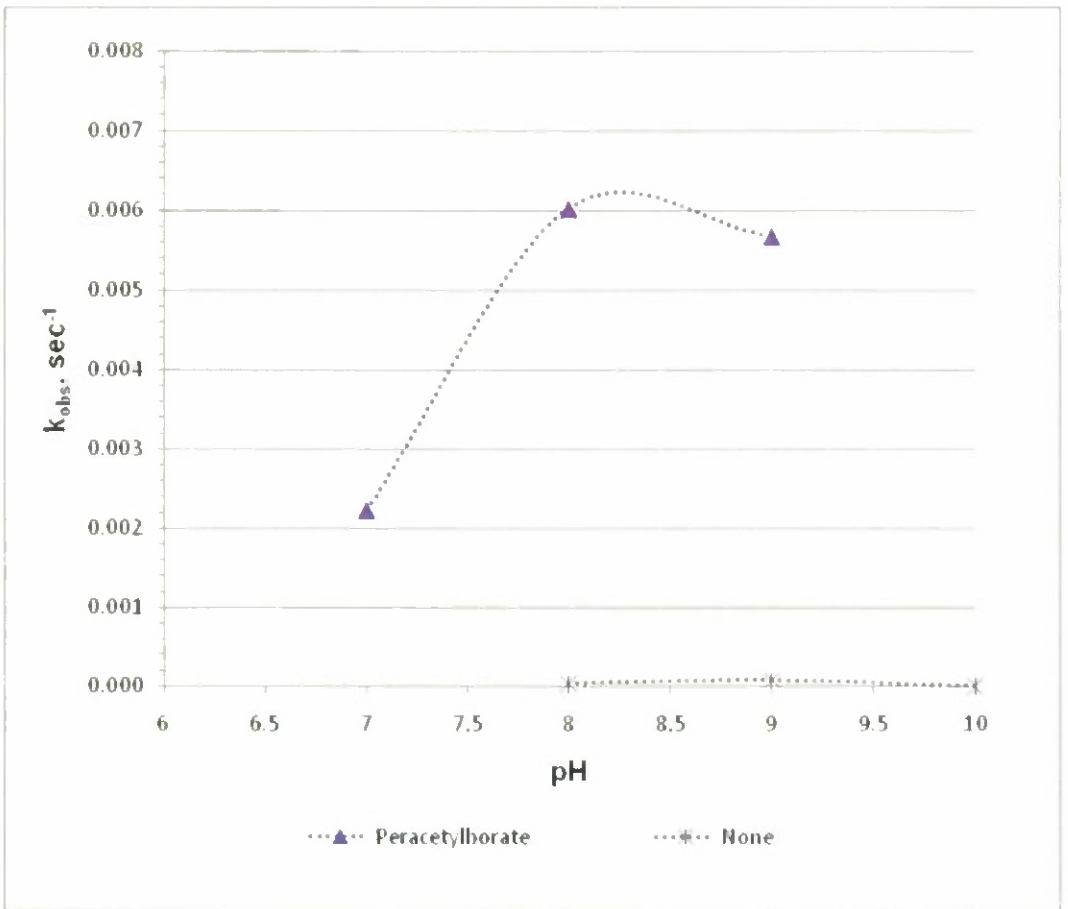
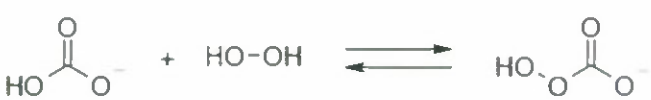


Figure 3. pH dependence of peracetylborate reaction with VX.

3.1.5 Peroxomonocarbonate

Peroxomonocarbonate (HCO_4-), also known as hydrogenperoxymonocarbonate, and peroxymonocarbonate, is formed from bicarbonate and hydrogen peroxide with a structure of $HOOCO_2$-. Bicarbonate anion and aqueous hydrogen peroxide establish equilibrium with peroxomonocarbonate, as shown in eq (5).



(5)

The pK_a of the hydroperoxy group in peroxycarboxylic acids is ca. 8, but pK_a = 11.6 for hydrogen peroxide in water so that HO_2- is formed only in solutions of relatively high pH, above those studied in these experiments. If the reaction of peroxomonocarbonate and HO_2- is followed

under conditions in which H_2O_2 is only partially deprotonated, e.g., with dilute OH- in excess over H_2O_2, pH conditions will affect both deprotonation of H_2O_2 and reactions involving HO_2-. These problems were avoided by keeping the hydrogen peroxide in excess over bicarbonate so that peroxomonocarbonate concentration is approximately given by the concentration of added bicarbonate, since the equilibrium between hydrogen peroxide and peroxomonocarbonate anion strongly favors the latter as shown in eq (5).

The generation of peroxomonocarbonate was studied by Suess and Janik by mixing ^{13}C enriched sodium bicarbonate with a 20-fold excess of hydrogen peroxide in D_2O and monitored by ^{13}C NMR.[11] The equilibrium was reported to be complete within approximately 25 min at 30°C, with almost 80% conversion to the peroxomonocarbonate as shown in Figure 4.

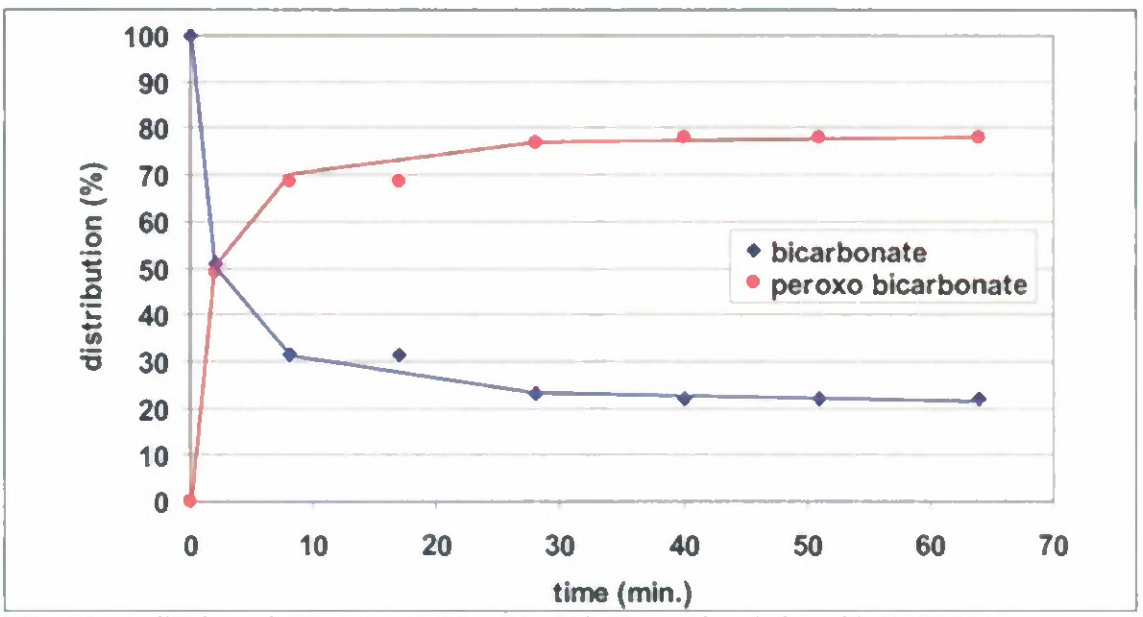


Figure 4. Equilibrium of peroxomonocarbonate and bicarbonate in solution with excess H_2O_2. (copied from www.tappsa.co.za)

Similar procedures and ratios of bicarbonate and peroxide were used by Richardson et. al. to generate peroxomonocarbonate for sulfide reaction studies.[12] In the presence of excess hydrogen peroxide, the peroxomonocarbonate concentration was also shown to be steady for up to 5 h.[11] To evaluate the pH dependence on the reaction with VX, peroxomonocarbonate was prepared in aqueous solution containing 0.1 M bicarbonate and 1 M hydrogen peroxide with a 25 min equilibration period prior to mixing with VX substrate to ensure the complete pre-equilibration of peroxomonocarbonate formation for each kinetic run. The pH was maintained using 0.5 M sodium phosphate monobasic/dibasic or sodium phosphate dibasic/sodium hydroxide buffer media.

The observed reaction rate of VX in the peroxomonocarbonate/hydrogen peroxide solution, shown in Figure 5, increased sharply in the pH range from 8 to 10.

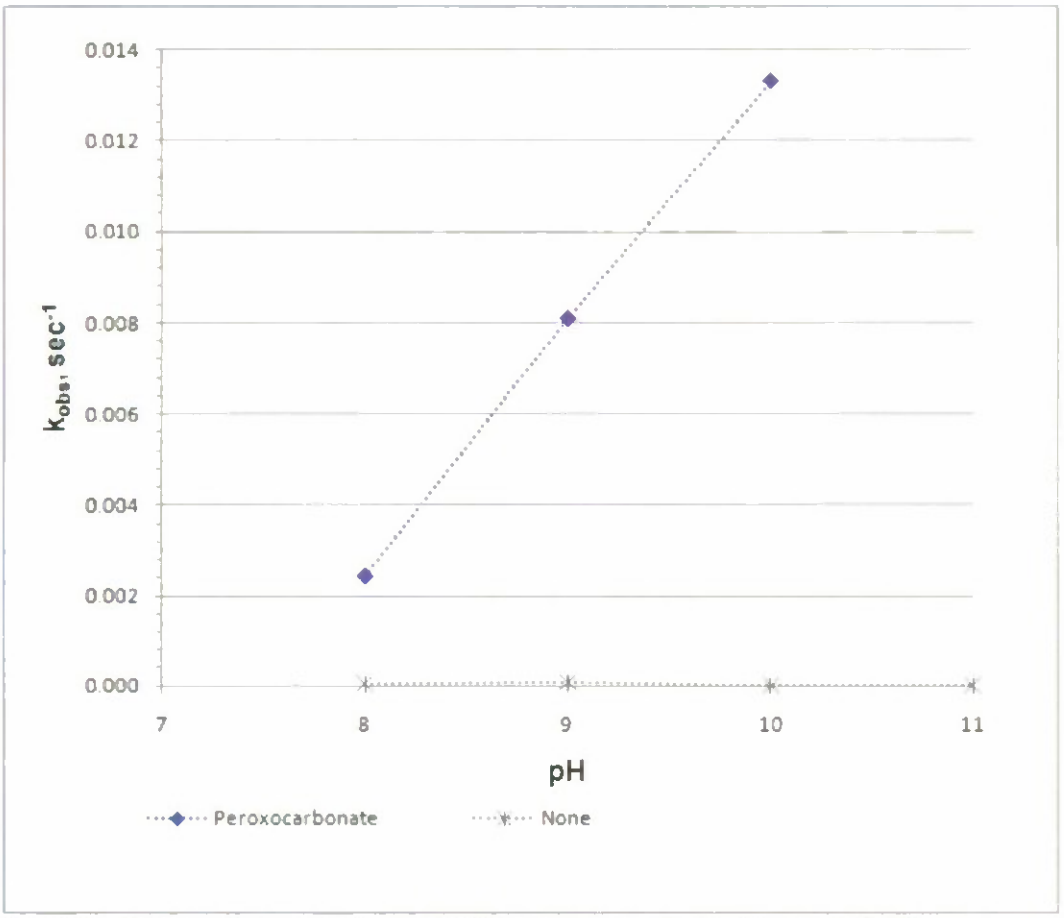


Figure 5. pH dependence of peroxomonocarbonate/H_2O_2 and H_2O_2 reactions with VX.

3.1.6 Percarbonate

Sodium percarbonate is an adduct of sodium carbonate and hydrogen peroxide, as shown in Figure 6, with formula $Na_2CO_3 \cdot 1.5\ H_2O_2$. Unlike sodium perborate, sodium percarbonate contains hydrogen peroxide in the solid state.

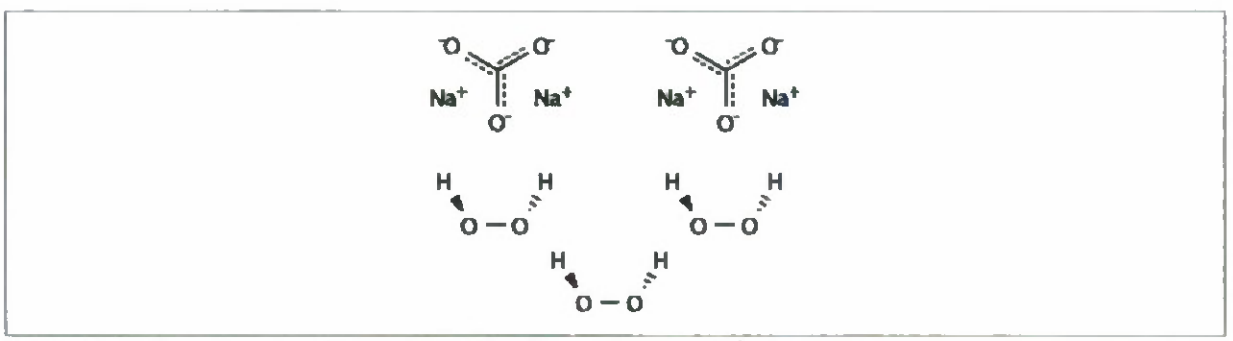


Figure 6. Sodium percarbonate, an adduct of sodium carbonate and hydrogen peroxide.

An X-ray study of the crystal structure of sodium percarbonate has revealed that hydrogen peroxide is found whole, encapsulated by hydrogen bonds in a Na_2CO_3 matrix. Sodium percarbonate dissolves in water to release hydrogen peroxide.[13] In aqueous solution, the dominant chemistry of percarbonate deviates little from that of alkaline hydrogen peroxide. Any enhancement of reactivity is most probably attributable to the presence of the peroxocarbonate anion.[6]

The observed reaction rate of VX in the percarbonate solutions shown in Figure 7 showed a near steady increase as the pH rose from 8 to 12.

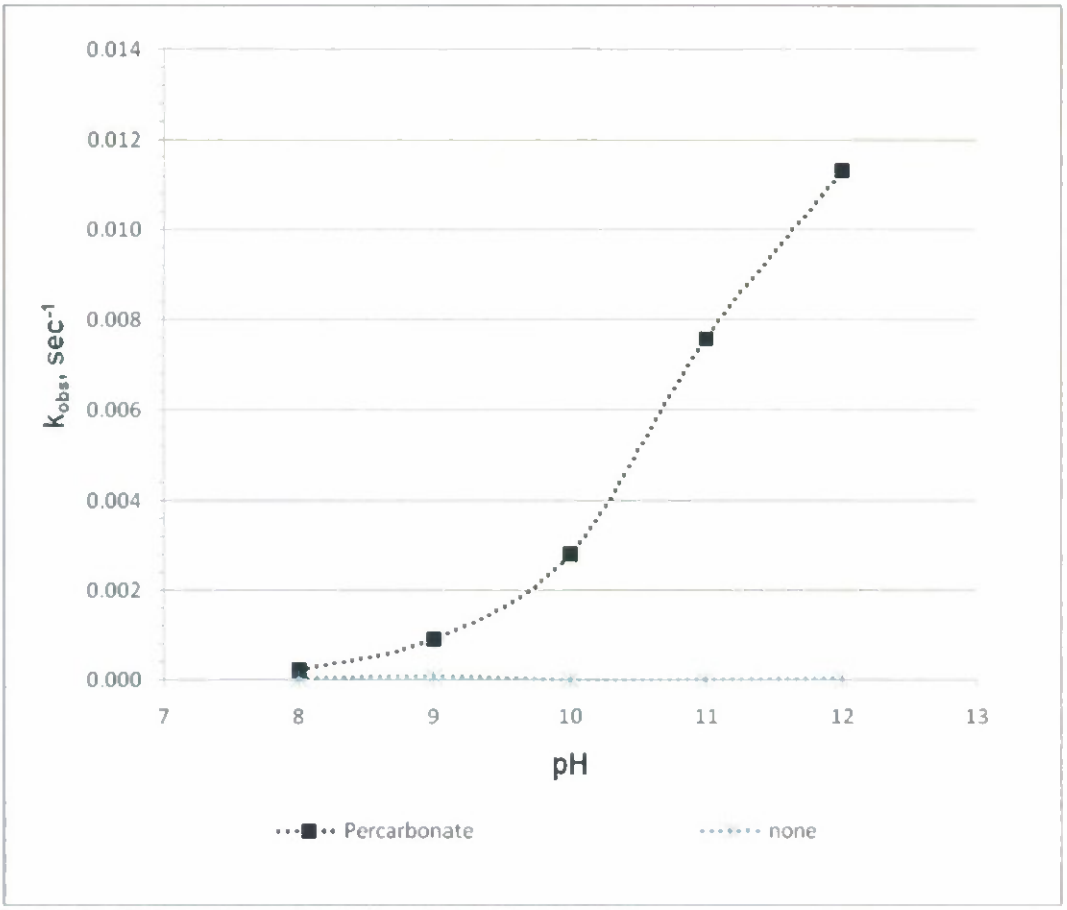


Figure 7. pH dependence of percarbonate reaction with VX.

3.1.7 VX Reaction Rate pH Dependence Discussion

The pH dependence of the observed VX reaction rates in oxidant solutions is summarized in Table 8 and Figure 8. The data are also presented as VX reaction half-lives in Table 9 and Figure 9.

Table 8. Observed reaction rate of 0.005M VX in 0.1M oxidant.

pH	Observed Rate Constant (k_{obs}, s^{-1})					
	Peracetic acid	Peroxo-monocarbonate /1M H_2O_2	Percarbonate	Peroxoborate	Peracetylborate	None
6	-3.37E-04	---	---	---	---	---
7	-2.44E-03	---	---	---	-2.22E-03	---
8	-1.80E-02	-2.44E-03	-2.22E-04	-1.52E-04	-6.02E-03	-3.49E-05
9	-3.05E-02	-8.09E-03	-9.22E-04	-4.79E-04	-5.67E-03	-7.66E-05
10	-8.30E-03	-1.33E-02	-2.82E-03	-9.62E-04	---	-1.77E-06
11	-2.41E-03	---	-7.58E-03	-2.43E-03	---	-9.16E-06
12	---	---	-1.13E-02	-1.07E-02	---	-2.26E-05

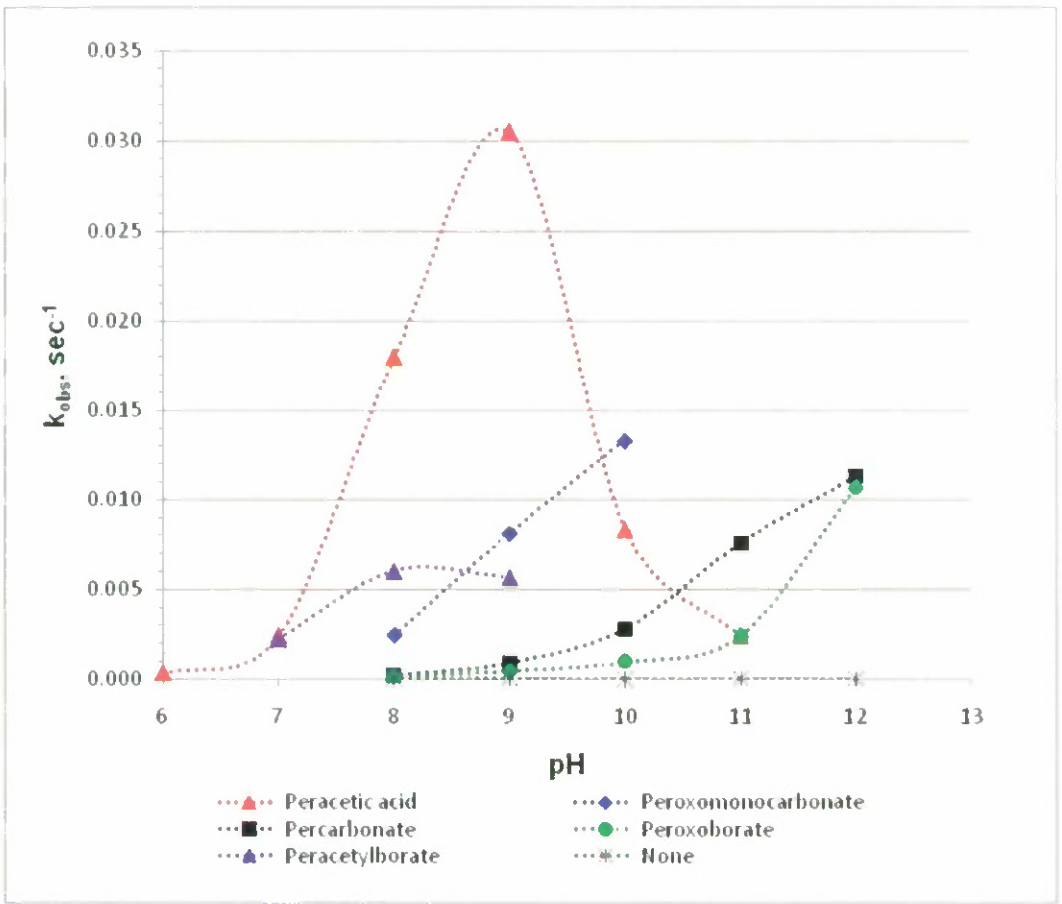


Figure 8. Observed reaction rate of 0.005M VX in 0.1M oxidant.

Table 9. Half-life of 0.005M VX in 0.1M oxidant.

pH	Half-life (min)					
	Peracetic acid	Peroxo-monocarbonate /1M H_2O_2	Percarbonate	Peroxoborate	Peracetylborate	None
6	34.3	---	---	---	---	---
7	4.7	---	---	---	5.2	---
8	0.6	4.7	52.0	76.0	1.9	331.0
9	0.4	1.4	12.5	24.1	2.0	150.8
10	1.4	0.9	4.1	12.0	---	6526.8
11	4.8	---	1.5	4.8	---	1261.2
12	---	---	1.0	1.1	---	511.2

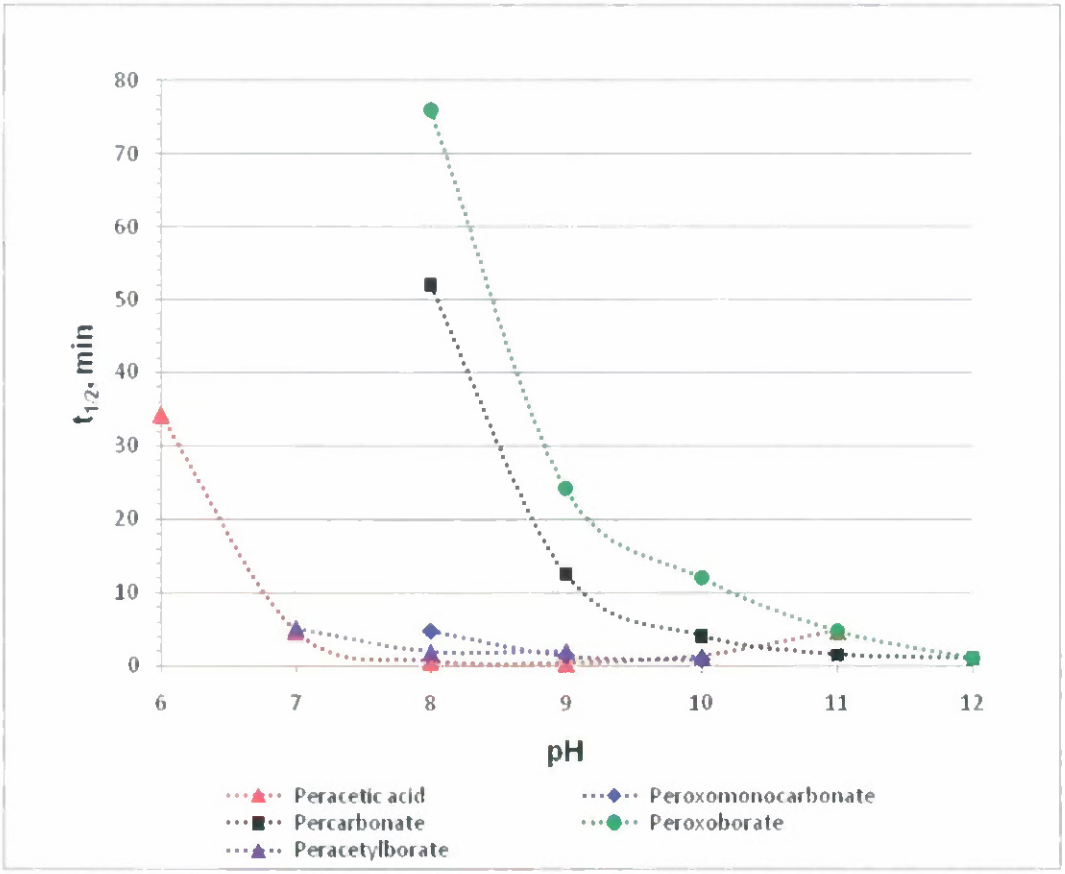


Figure 9. Half-life of 0.005M VX in 0.1M oxidant.

Using the peracetic acid, peracetylborate, and peroxomonocarbonate/hydrogen peroxide solutions provided the highest reactivity in the low alkaline range (pH 8–9). Percarbonate and peroxoborate were reactive with VX, but test results showed low reactivity in the pH 8–10 range, relative to the other oxidant solutions. With the exception of peracetic acid and peracetylborate, results from all the oxidants tested showed greater reactivity in aqueous solutions as the pH increased.

Testing of peracetic acid showed the highest VX reaction rate with an optimal VX reactivity at pH 9, while the use of peracetylborate showed an optimal rate in solutions at pH 8. Although peracetylborate acts as a source of peracetic acid, the differences revealed in the observed rate constants between the peracetylborate and the peracetic acid solutions may be due to the availability of peracetic acid provided in the peracetylborate solution. The free peracetic acid available for reaction in the peracetylborate solution will exist in equilibrium with that bound to the borate core, and the lower effective concentration may relate to the lower observed rate constant. In contrast, all of the peracetic acid will be available for reaction in the peracetic acid solution.

The background VX observed reaction rate, in the absence of a reactive oxidant, was very low and had an insignificant contribution relative to the VX reactivity observed in the presence of a reactive constituent.

3.2 Surfactant Effect on Spore Removal

3.2.1 Objective

Three representative surfactant types (non-ionic, anionic, and cationic) were studied to compare their ability to remove *Bacillus anthracis* ΔSterne spores from glass, chemical agent resistant coating (CARC), and rubber surfaces.

3.2.2 Results and Discussion

Aqueous solutions containing 0.01 wt % surfactants, in addition to water without surfactant as a control, were evaluated for spore removal efficacy as a function of surfactant type from CARC, rubber, and glass surfaces. Surfactants (Tween 80, sodium dodecyl sulfate [SDS], and cetyl trimethyl ammonium bromide [CTAB]) representing each surfactant type (non-ionic, anionic, and cationic, respectively) were tested. Since the removal process used in testing consisted of vortexing surfactant solutions, and was not directly applicable to a fielded spray system, the resulting removal data was used to assess the relative ranking of the surfactants, and not for determination of absolute spore removal efficacy.

The spore recovery results using water (no surfactant) are summarized in Table 10 through Table 12 for glass, CARC, and rubber, respectively.

Table 10. Spore recovery from glass using water.

Material	Sample	Dilution	Plate Count	Dilution adjustment	Average Recovered Spores (cfu/mL)	Final Conc. (cfu/mL)	Standard Deviation (cfu/mL)
Glass		1.00E+03	50	1.00E+06	1.13E+06	8.27E+05	1.70E+05
Glass	1	1.00E+03	60	1.20E+06			
Glass		1.00E+03	59	1.18E+06			
Glass		1.00E+03	30	6.00E+05	7.33E+05		
Glass	2	1.00E+03	42	8.40E+05			
Glass		1.00E+03	38	7.60E+05			
Glass		1.00E+03	35	7.00E+05	7.93E+05		
Glass	3	1.00E+03	44	8.80E+05			
Glass		1.00E+03	40	8.00E+05			
Glass		1.00E+03	32	6.40E+05	7.53E+05		
Glass	4	1.00E+03	30	6.00E+05			
Glass		1.00E+03	51	1.02E+06			
Glass		1.00E+03	44	8.80E+05	7.27E+05		
Glass	5	1.00E+03	29	5.80E+05			
Glass		1.00E+03	36	7.20E+05			

Table 11. Spore recovery from CARC using water.

Material	Sample	Dilution	Plate Count	Dilution adjustment	Average Recovered Spores (cfu/mL)	Final Conc. (cfu/mL)	Standard Deviation (cfu/mL)
CARC		1.00E+03	26	5.20E+05	5.20E+05	5.96E+05	5.00E+04
CARC	1	1.00E+03	28	5.60E+05			
CARC		1.00E+03	24	4.80E+05			
CARC		1.00E+03	30	6.00E+05	6.20E+05		
CARC	2	1.00E+03	31	6.20E+05			
CARC		1.00E+03	32	6.40E+05			
CARC		1.00E+03	24	4.80E+05	6.07E+05		
CARC	3	1.00E+03	32	6.40E+05			
CARC		1.00E+03	35	7.00E+05			
CARC		1.00E+03	37	7.40E+05	5.80E+05		
CARC	4	1.00E+03	24	4.80E+05			
CARC		1.00E+03	26	5.20E+05			
CARC		1.00E+03	30	6.00E+05	6.53E+05		
CARC	5	1.00E+03	37	7.40E+05			
CARC		1.00E+03	31	6.20E+05			

Table 12. Spore recovery from rubber using water.

Material	Sample	Dilution	Plate Count	Dilution adjustment	Average Recovered Spores (cfu/mL)	Final Conc. (cfu/mL)	Standard Deviation (cfu/mL)
Rubber		1.00E+03	54	1.08E+06			
Rubber	1	1.00E+03	79	1.58E+06	1.30E+06		
Rubber		1.00E+03	62	1.24E+06			
Rubber		1.00E+03	54	1.08E+06			
Rubber	2	1.00E+03	57	1.14E+06	1.13E+06		
Rubber		1.00E+03	59	1.18E+06			
Rubber		1.00E+03	54	1.08E+06			
Rubber	3	1.00E+03	60	1.20E+06	1.16E+06	1.16E+06	1.04E+05
Rubber		1.00E+03	60	1.20E+06			
Rubber		1.00E+03	50	1.00E+06			
Rubber	4	1.00E+03	47	9.40E+05	1.01E+06		
Rubber		1.00E+03	55	1.10E+06			
Rubber		1.00E+03	56	1.12E+06			
Rubber	5	1.00E+03	61	1.22E+06	1.20E+06		
Rubber		1.00E+03	63	1.26E+06			

The spore recovery results using Tween 80 are summarized in Table 13 through Table 15 for glass, CARC, and rubber, respectively.

Table 13. Spore recovery from glass using Tween 80.

Material	Sample	Dilution	Plate Count	Dilution adjustment	Average Recovered Spores (cfu/mL)	Final Conc. (cfu/mL)	Standard Deviation (cfu/mL)
Glass		1.00E+03	77	1.54E+06			
Glass	1	1.00E+03	59	1.18E+06	1.29E+06		
Glass		1.00E+03	57	1.14E+06			
Glass		1.00E+03	55	1.10E+06			
Glass	2	1.00E+03	63	1.26E+06	1.27E+06		
Glass		1.00E+03	72	1.44E+06			
Glass		1.00E+03	58	1.16E+06			
Glass	3	1.00E+03	61	1.22E+06	1.19E+06	1.32E+06	1.96E+05
Glass		1.00E+03	60	1.20E+06			
Glass		1.00E+03	83	1.66E+06			
Glass	4	1.00E+03	71	1.42E+06	1.66E+06		
Glass		1.00E+03	95	1.90E+06			
Glass		1.00E+03	56	1.12E+06			
Glass	5	1.00E+03	58	1.16E+06	1.19E+06		
Glass		1.00E+03	64	1.28E+06			

Table 14. Spore recovery from CARC using Tween 80.

Material	Sample	Dilution	Plate Count	Dilution adjustment	Average Recovered Spores (cfu/mL)	Final Conc. (cfu/mL)	Standard Deviation (cfu/mL)
CARC		1.00E+03	86	1.72E+06			
CARC	1	1.00E+03	97	1.94E+06	1.79E+06		
CARC		1.00E+03	85	1.70E+06			
CARC		1.00E+03	89	1.78E+06			
CARC	2	1.00E+03	78	1.56E+06	1.63E+06		
CARC		1.00E+03	78	1.56E+06			
CARC		1.00E+03	78	1.56E+06			
CARC	3	1.00E+03	90	1.80E+06	1.63E+06	1.58E+06	2.13E+05
CARC		1.00E+03	76	1.52E+06			
CARC		1.00E+03	63	1.26E+06			
CARC	4	1.00E+03	65	1.30E+06	1.22E+06		
CARC		1.00E+03	55	1.10E+06			
CARC		1.00E+03	78	1.56E+06			
CARC	5	1.00E+03	83	1.66E+06	1.64E+06		
CARC		1.00E+03	85	1.70E+06			

Table 15. Spore recovery from rubber using Tween 80.

Material	Sample	Dilution	Plate Count	Dilution adjustment	Average Recovered Spores (cfu/mL)	Final Conc. (cfu/mL)	Standard Deviation (cfu/mL)
Rubber		1.00E+03	81	1.62E+06			
Rubber	1	1.00E+03	93	1.86E+06	1.67E+06		
Rubber		1.00E+03	76	1.52E+06			
Rubber		1.00E+03	90	1.80E+06			
Rubber	2	1.00E+03	87	1.74E+06	1.79E+06		
Rubber		1.00E+03	91	1.82E+06			
Rubber		1.00E+03	83	1.66E+06			
Rubber	3	1.00E+03	92	1.84E+06	1.72E+06	1.74E+06	4.66E+04
Rubber		1.00E+03	83	1.66E+06			
Rubber		1.00E+03	84	1.68E+06			
Rubber	4	1.00E+03	91	1.82E+06	1.77E+06		
Rubber		1.00E+03	90	1.80E+06			
Rubber		1.00E+03	94	1.88E+06			
Rubber	5	1.00E+03	74	1.48E+06	1.75E+06		
Rubber		1.00E+03	94	1.88E+06			

The spore recovery results using SDS are summarized in Table 16 through Table 18 for glass, CARC, and rubber, respectively.

Table 16. Spore recovery from glass using SDS.

Material	Sample	Dilution	Plate Count	Dilution adjustment	Average Recovered Spores (cfu/mL)	Final Conc. (cfu/mL)	Standard Deviation (cfu/mL)
Glass		1.00E+03	101	2.02E+06			
Glass	1	1.00E+03	92	1.84E+06	1.79E+06		
Glass		1.00E+03	76	1.52E+06			
Glass		1.00E+03	78	1.56E+06			
Glass	2	1.00E+03	79	1.58E+06	1.65E+06		
Glass		1.00E+03	90	1.80E+06			
Glass		1.00E+03	76	1.52E+06			
Glass	3	1.00E+03	82	1.64E+06	1.63E+06	1.63E+06	1.02E+05
Glass		1.00E+03	86	1.72E+06			
Glass		1.00E+03	77	1.54E+06			
Glass	4	1.00E+03	90	1.80E+06	1.59E+06		
Glass		1.00E+03	72	1.44E+06			
Glass		1.00E+03	75	1.50E+06			
Glass	5	1.00E+03	69	1.38E+06	1.51E+06		
Glass		1.00E+03	83	1.66E+06			

Table 17. Spore recovery from CARC using SDS.

Material	Sample	Dilution	Plate Count	Dilution adjustment	Average Recovered Spores (cfu/mL)	Final Conc. (cfu/mL)	Standard Deviation (cfu/mL)
CARC		1.00E+03	95	1.90E+06			
CARC	1	1.00E+03	76	1.52E+06	2.02E+06		
CARC		1.00E+03	132	2.64E+06			
CARC		1.00E+03	91	1.82E+06			
CARC	2	1.00E+03	75	1.50E+06	1.73E+06		
CARC		1.00E+03	94	1.88E+06			
CARC		1.00E+03	99	1.98E+06			
CARC	3	1.00E+03	100	2.00E+06	1.93E+06	1.87E+06	1.59E+05
CARC		1.00E+03	91	1.82E+06			
CARC		1.00E+03	108	2.16E+06			
CARC	4	1.00E+03	97	1.94E+06	1.99E+06		
CARC		1.00E+03	94	1.88E+06			
CARC		1.00E+03	76	1.52E+06			
CARC	5	1.00E+03	92	1.84E+06	1.67E+06		
CARC		1.00E+03	82	1.64E+06			

Table 18. Spore recovery from rubber using SDS.

Material	Sample	Dilution	Plate Count	Dilution adjustment	Average Recovered Spores (cfu/mL)	Final Conc. (cfu/mL)	Standard Deviation (cfu/mL)
Rubber		1.00E+03	101	2.02E+06			
Rubber	1	1.00E+03	88	1.76E+06	1.85E+06		
Rubber		1.00E+03	89	1.78E+06			
Rubber		1.00E+03	107	2.14E+06			
Rubber	2	1.00E+03	116	2.32E+06	2.13E+06		
Rubber		1.00E+03	97	1.94E+06			
Rubber		1.00E+03	107	2.14E+06			
Rubber	3	1.00E+03	123	2.46E+06	2.16E+06	2.09E+06	1.48E+05
Rubber		1.00E+03	94	1.88E+06			
Rubber		1.00E+03	112	2.24E+06			
Rubber	4	1.00E+03	121	2.42E+06	2.07E+06		
Rubber		1.00E+03	77	1.54E+06			
Rubber		1.00E+03	117	2.34E+06			
Rubber	5	1.00E+03	122	2.44E+06	2.25E+06		
Rubber		1.00E+03	98	1.96E+06			

The spore recovery results using CTAB are summarized in Table 19 through Table 21 for glass, CARC, and rubber, respectively.

Table 19. Spore recovery from glass using CTAB.

Material	Sample	Dilution	Plate Count	Dilution adjustment	Average Recovered Spores (cfu/mL)	Final Conc. (cfu/mL)	Standard Deviation (cfu/mL)
Glass		1.00E+03	49	1.23E+06			
Glass	1	1.00E+03	58	1.45E+06	1.32E+06		
Glass		1.00E+03	51	1.28E+06			
Glass		1.00E+03	61	1.53E+06			
Glass	2	1.00E+03	63	1.58E+06	1.62E+06		
Glass		1.00E+03	70	1.75E+06			
Glass		1.00E+03	46	1.15E+06			
Glass	3	1.00E+03	44	1.10E+06	1.03E+06		
Glass		1.00E+03	33	8.25E+05			
Glass		1.00E+03	31	7.75E+05			
Glass	4	1.00E+03	43	1.08E+06	1.01E+06		
Glass		1.00E+03	47	1.18E+06			
Glass		1.00E+03	33	8.25E+05			
Glass	5	1.00E+03	46	1.15E+06	9.83E+05		
Glass		1.00E+03	39	9.75E+05			

Table 20. Spore recovery from CARC using CTAB.

Material	Sample	Dilution	Plate Count	Dilution adjustment	Average Recovered Spores (cfu/mL)	Final Conc. (cfu/mL)	Standard Deviation (cfu/mL)
CARC		1.00E+03	47	1.18E+06			
CARC	1	1.00E+03	53	1.33E+06	1.19E+06		
CARC		1.00E+03	43	1.08E+06			
CARC		1.00E+03	61	1.53E+06			
CARC	2	1.00E+03	67	1.68E+06	1.47E+06		
CARC		1.00E+03	48	1.20E+06			
CARC		1.00E+03	51	1.28E+06			
CARC	3	1.00E+03	35	8.75E+05	1.08E+06	1.18E+06	2.89E+05
CARC		1.00E+03	43	1.08E+06			
CARC		1.00E+03	55	1.38E+06			
CARC	4	1.00E+03	62	1.55E+06	1.42E+06		
CARC		1.00E+03	53	1.33E+06			
CARC		1.00E+03	23	5.75E+05			
CARC	5	1.00E+03	44	1.10E+06	7.50E+05		
CARC		1.00E+03	23	5.75E+05			

Table 21. Spore recovery from rubber using CTAB.

Material	Sample	Dilution	Plate Count	Dilution adjustment	Average Recovered Spores (cfu/mL)	Final Conc. (cfu/mL)	Standard Deviation (cfu/mL)
Rubber		1.00E+03	67	1.68E+06			
Rubber	1	1.00E+03	65	1.63E+06	1.61E+06		
Rubber		1.00E+03	61	1.53E+06			
Rubber		1.00E+03	62	1.55E+06			
Rubber	2	1.00E+03	73	1.83E+06	1.91E+06		
Rubber		1.00E+03	94	2.35E+06			
Rubber		1.00E+03	88	2.20E+06			
Rubber	3	1.00E+03	97	2.43E+06	2.19E+06	1.92E+06	2.47E+05
Rubber		1.00E+03	78	1.95E+06			
Rubber		1.00E+03	65	1.63E+06			
Rubber	4	1.00E+03	67	1.68E+06	1.77E+06		
Rubber		1.00E+03	80	2.00E+06			
Rubber		1.00E+03	88	2.20E+06			
Rubber	5	1.00E+03	70	1.75E+06	2.14E+06		
Rubber		1.00E+03	99	2.48E+06			

The average spore recoveries for the three surfactant solutions and the water control are presented in Table 22. These average spore recoveries values equate to the average spore removal provided by the surfactant solutions, since the spores recovered were those removed from the materials.

Table 22. Summary log number average spore recoveries.

Surfactant	Material	Average Log Number Recovered Spores					
		Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Average
None (Water only)	Glass	1.13E+06	7.33E+05	7.93E+05	7.53E+05	7.27E+05	8.27E+05
None (Water only)	CARC	5.20E+05	6.20E+05	6.07E+05	5.80E+05	6.53E+05	5.96E+05
None (Water only)	Rubber	1.30E+06	1.13E+06	1.16E+06	1.01E+06	1.20E+06	1.16E+06
Tween 80	Glass	1.29E+06	1.27E+06	1.19E+06	1.66E+06	1.19E+06	1.32E+06
Tween 80	CARC	1.79E+06	1.63E+06	1.63E+06	1.22E+06	1.64E+06	1.58E+06
Tween 80	Rubber	1.67E+06	1.79E+06	1.72E+06	1.77E+06	1.75E+06	1.74E+06
SDS	Glass	1.79E+06	1.65E+06	1.63E+06	1.59E+06	1.51E+06	1.63E+06
SDS	CARC	2.02E+06	1.73E+06	1.93E+06	1.99E+06	1.67E+06	1.87E+06
SDS	Rubber	1.85E+06	2.13E+06	2.16E+06	2.07E+06	2.25E+06	2.09E+06
CTAB	Glass	1.32E+06	1.62E+06	1.03E+06	1.01E+06	9.83E+05	1.19E+06
CTAB	CARC	1.19E+06	1.47E+06	1.08E+06	1.42E+06	7.50E+05	1.18E+06
CTAB	Rubber	1.61E+06	1.91E+06	2.19E+06	1.77E+06	2.14E+06	1.92E+06

As shown in Figure 10, results from the anionic surfactant, SDS, provided the highest level of spore removal from all the surfaces, followed by the non-ionic surfactant, Tween 80, on glass and CARC surfaces. On glass and CARC surfaces, test results using SDS and Tween 80 provided higher level of removal than CTAB; however testing CTAB resulted in a slightly higher level of removal than Tween 80 on rubber. All the surfactant solutions outperformed the water control.

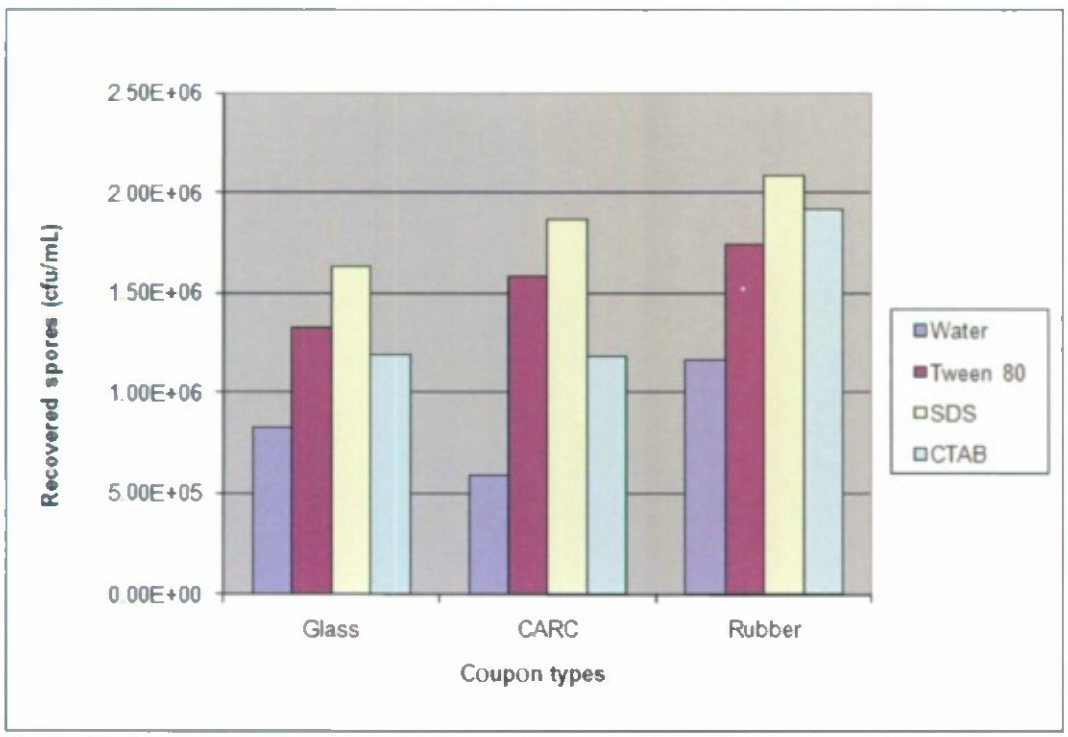


Figure 10. *B. anthracis* ΔSteme spore recovery from panels by 0.01% surfactant solutions.

The average percent spore recoveries for the three surfactant solutions and the water control, are presented in Table 23.

Table 23. Summary percent average spore recoveries.

Surfactant	Material	Average Percent Recovered Spores					
		Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Average
None (Water only)	Glass	11.3	7.3	7.9	7.5	7.3	8.3
None (Water only)	CARC	5.2	6.2	6.1	5.8	6.5	6.0
None (Water only)	Rubber	13.0	11.3	11.6	10.1	12.0	11.6
Tween 80	Glass	12.9	12.7	11.9	16.6	11.9	13.2
Tween 80	CARC	17.9	16.3	16.3	12.2	16.4	15.8
Tween 80	Rubber	16.7	17.9	17.2	17.7	17.5	17.4
SDS	Glass	17.9	16.5	16.3	15.9	15.1	16.3
SDS	CARC	20.2	17.3	19.3	19.9	16.7	18.7
SDS	Rubber	18.5	21.3	21.6	20.7	22.5	20.9
CTAB	Glass	13.2	16.2	10.3	10.1	9.8	11.9
CTAB	CARC	11.9	14.7	10.8	14.2	7.5	11.8
CTAB	Rubber	16.1	19.1	21.9	17.7	21.4	19.2

As shown in Figure 11, the percent removal of the applied spores in the surfactant solutions is approximately 20% or less. Therefore, 80% or more of the spores are presumed to be associated with the panels following the 2 min pulsed-vortex procedure.

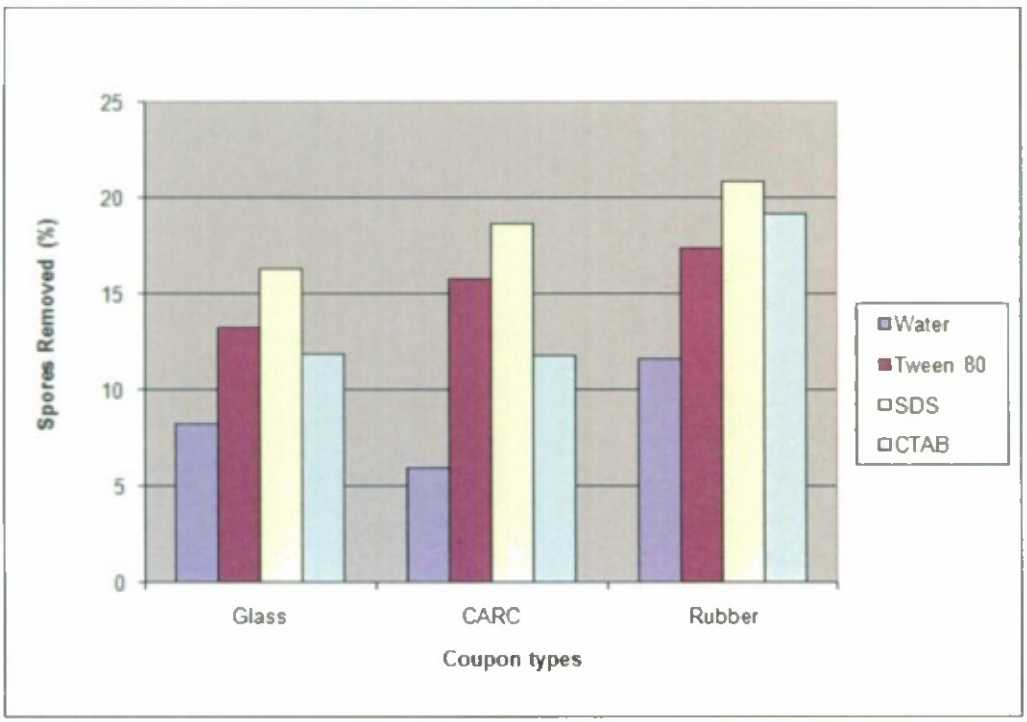


Figure 11. Average percent recovery *of B. anthracis* ΔSterne spore recovery from panels by 0.01% surfactant solutions.

The low percentage removal of *Bacillus anthracis* ΔSterne spore removal from the surfaces may, to some degree, be associated with the lower concentration of surfactant and/or the absence of buffered peptone used in the spore recovery solution. During previous development of sampling protocols, a significant difference between the extraction processes for two spore types being studied was reported. Extraction of *B. anthracis* ΔSterne spores required use of buffered peptone with surfactant for high recovery, while spores of *B. subtilis* required only water.[2] This difference could be due to differences in surface charge and/or hydrophobicity of the two spore types, and may account partially for the low recovery observed in these tests because buffered peptone was not used in the spore recovery solution.

3.3 Surfactant Effect on HD Emulsification

3.3.1 HD Emulsification as a Function of HLB

Because it is an extremely hydrophobic organic agent, HD is much more difficult to remove from surfaces using water when compared with the agents VX and GD. The addition of surfactants can dramatically improve the ability of aqueous solutions to emulsify HD and aid in its removal. The relationship between the surfactant hydrophilic-lipophilic balance (HLB number) and its ability to emulsify HD was studied.

Correlation of HLB value to the emulsification of HD will allow greater control of emulsification and enhanced removal of HD using aqueous systems. The HLB number is a scale based on the relative percentage of hydrophilic to lipophilic groups in the surfactant molecule. Table 24, taken from *Applied Surfactants: Principles and Applications* by T.F. Tadros,[14] provides a general guide to the selection of surfactants for a particular application, based on the HLB range.

Table 24. Summary of HLB Ranges and their Applications.

HLB Range	Application
3–6	W/O emulsifier
7–9	Wetting agent
8–18	O/W emulsifier
13–15	Detergent
15–18	Solubilizer

Emulsification was related to HLB using two different surfactant systems, a polyoxyethylene polysorbates (Span/Tween) system and a secondary alcohol ethoxylates (15-S Tergitols) system.

The HLB system is a useful tool for finding a suitable emulsifying system. To emulsify a mixture of water and oil such as HD, one or more emulsifiers are required. Each surfactant system can be characterized by an HLB value. This value depends on the nature of the oil and the product application. The application where water dominates and the oil forms droplets is designated as an O/W system. The HLB system predicts the optimum emulsion stability when the HLB value of the surfactant systems matches the required HLB of the O/W system. The required HLB is the value at which enhanced emulsion stability can, therefore, be attained.

The theoretical HLB value for a mixture of surfactants is given by eq (6):

$$HLB_{mixture} = x_1HLB_1 + x_2HLB_2 \quad (6)$$

where x_1, and x_2 are the weight fraction of the two surfactants with HLB_1 and HLB_2. Binary mixtures of non-ionic surfactants were prepared to yield a range of HLB values.

Tergitol solutions, with HLB values in the 10 to 15 range, provided the maximum emulsification of HD as shown in Figure 12. Solutions in this range provided approximately 60% emulsification of the HD. Emulsification provided by the Tergitol surfactant blends decreased sharply at HLB values above or below this range.

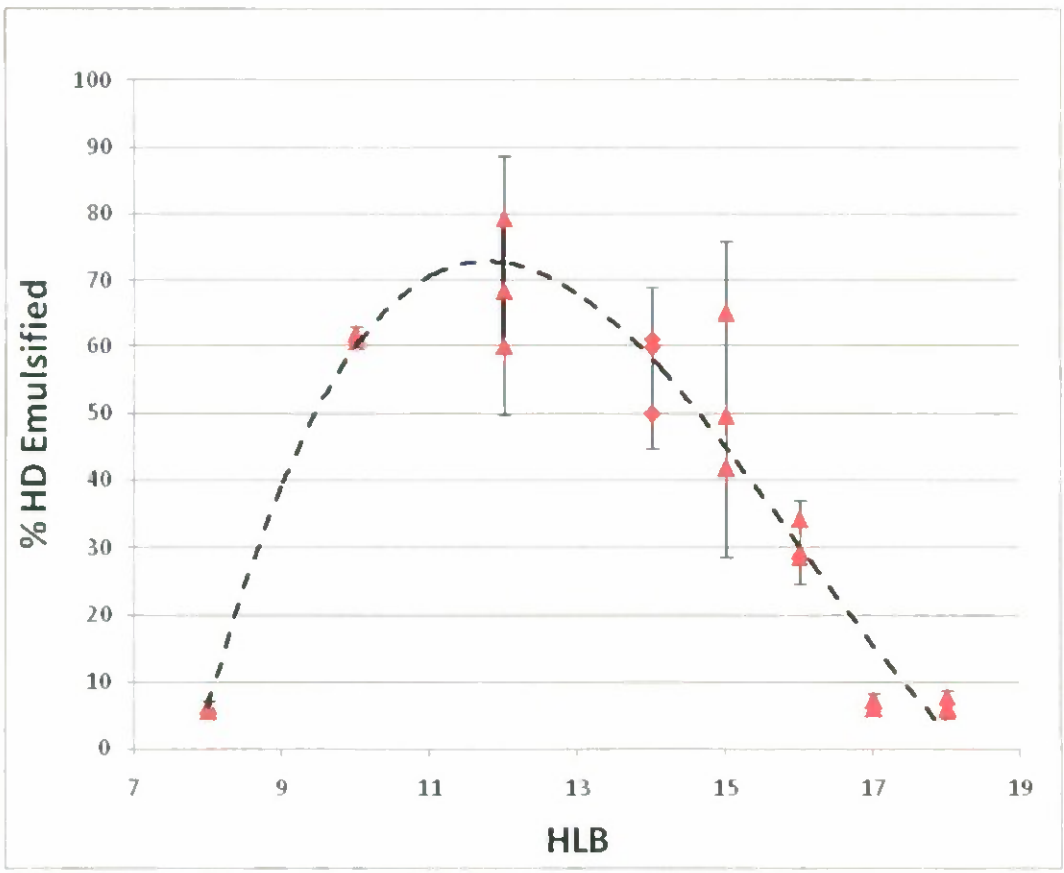


Figure 12. Emulsification of HD by Tergitol surfactants.

Span/Tween solutions resulted in a broader range of HLB values, providing maximum emulsification of HD, as shown in Figure 13, when compared with the Tergitol solutions. Solutions with HLB values ranging from 6 to 14 provided approximately 60% emulsification of the HD. Emulsification provided by the Span/Tween surfactant blends decreased sharply at HLB values below this range, but retained fairly good HD emulsification at values up to 17.

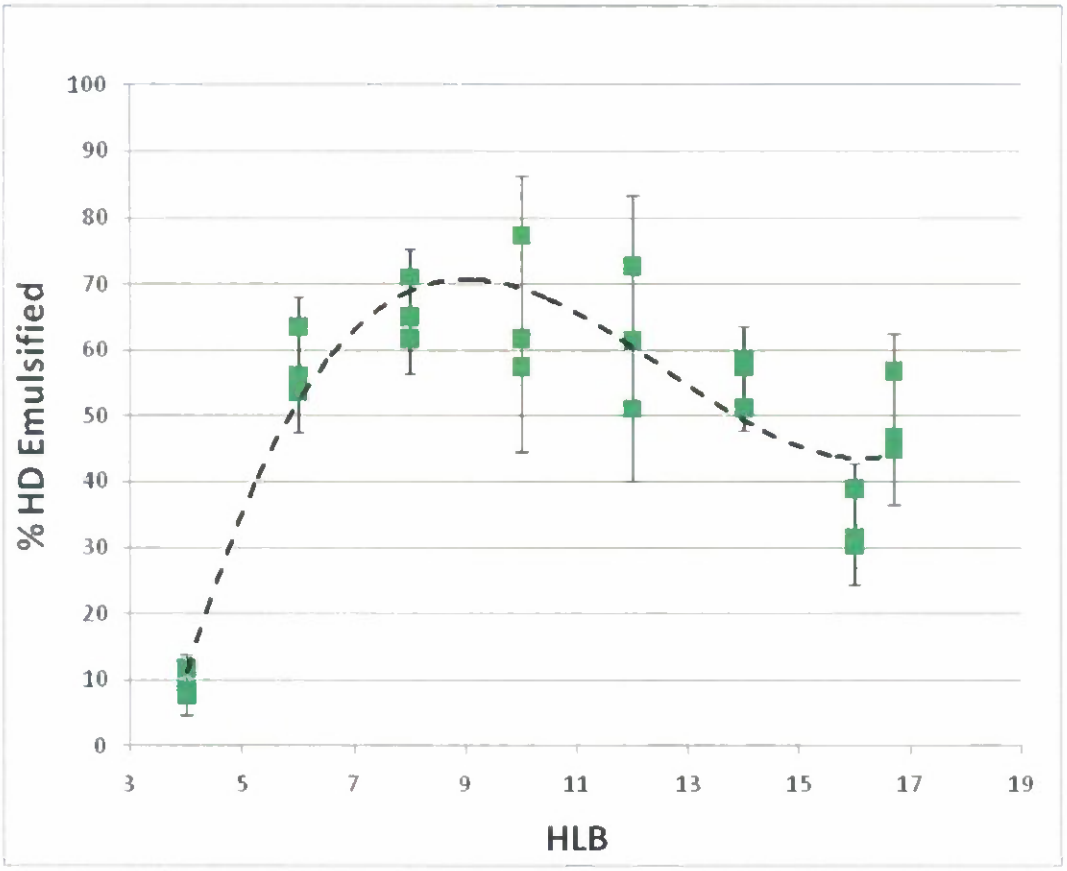


Figure 13. Emulsification of HD by Span/Tween surfactants.

An optimal HD emulsification range was selected from the overlap where the use of the two surfactant systems provided optimal performance. This was the range from 10 to 14 HLB, which is encompassed by the 8-18 HLB range suggested in Table 24 for O/W emulsification.

3.3.2 Emulsification as a Function of Surfactant Concentration and Static Period

Additional emulsion experiments were conducted to determine the percentage of the applied HD that was emulsified as a function of the surfactant concentration. The test solutions were prepared from a binary blend of 0.60 weight fraction Tergitol 15-S-3 and 0.40 weight fraction Tergitol 15-S-40. These surfactants had a calculated theoretical HLB value of 12, which was the midpoint of the 10 to 14 optimal range for HP emulsification. Surfactant concentrations ranging from 0.5 to 10 wt % were tested with the same procedure used to determine emulsification. In addition to a 1 min static period, a 4 h static period was also tested for determining emulsification.

The percent HD emulsified after sitting static for a period of 1 min increased logarithmically until leveling off at a maximum value of about 85% in aqueous solutions containing 6 to 10 wt % surfactant as shown in Figure 14.

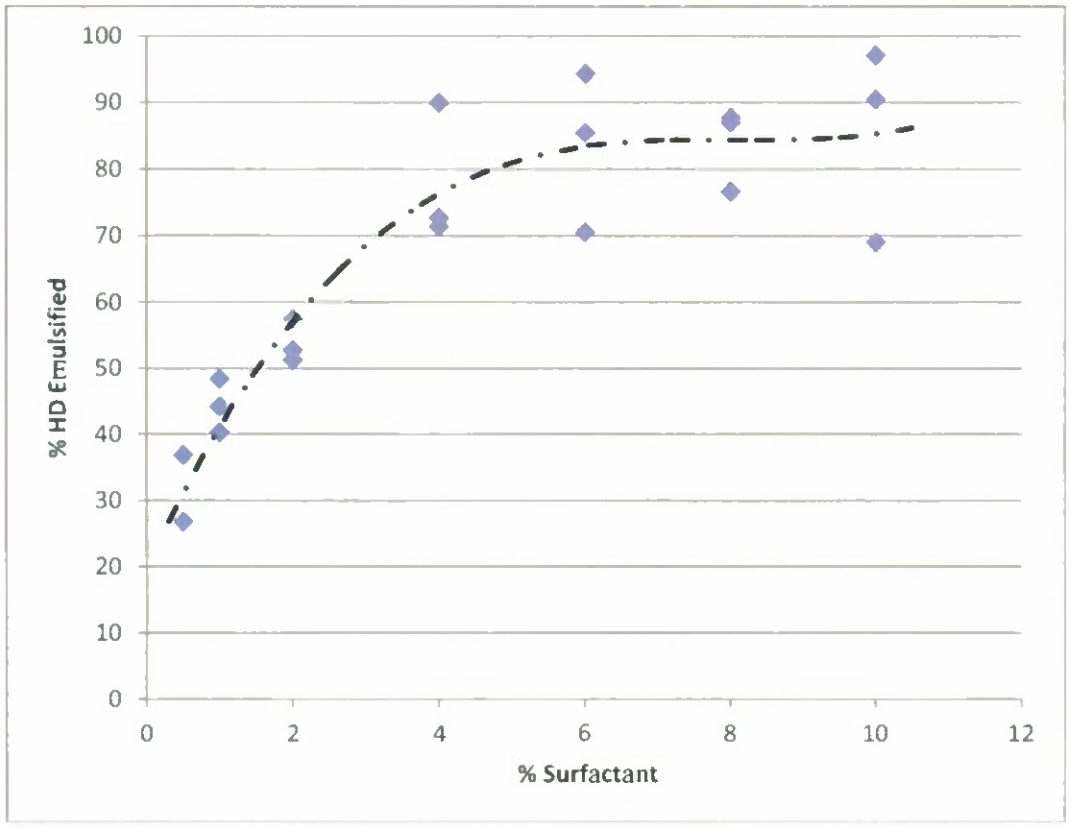


Figure 14. Emulsification of HD as a function of surfactant concentration following a short static period.

Although the emulsified HD remained suspended in the micelle during this short static period, the percent remaining emulsified was anticipated to decrease with a substantially longer static period. From a generalized decontamination process perspective, the 1 min static period corresponded to the removal process time while decontaminant is applied, while the 4 h static period corresponded to the time the collected runoff remains in a runoff collection vessel before neutralization treatment.

HD emulsification was also determined after a much longer static period of 4 h. Figure 15 shows the percent HD emulsified increased exponentially as the surfactant concentration is increased. As anticipated, lower percent HD emulsification was observed with the longer static period relative to the shorter static period because the emulsified HD droplets may coalesce over longer periods of time, getting larger and dropping out of the micelle. The solution containing 10% surfactant provided emulsification of 25% of the HD. In contrast to the HD emulsification during a short static period, increases in the surfactant concentration provided a greater increase in HD emulsification with a long static period as the surfactant concentration increased from 4 to 10%.

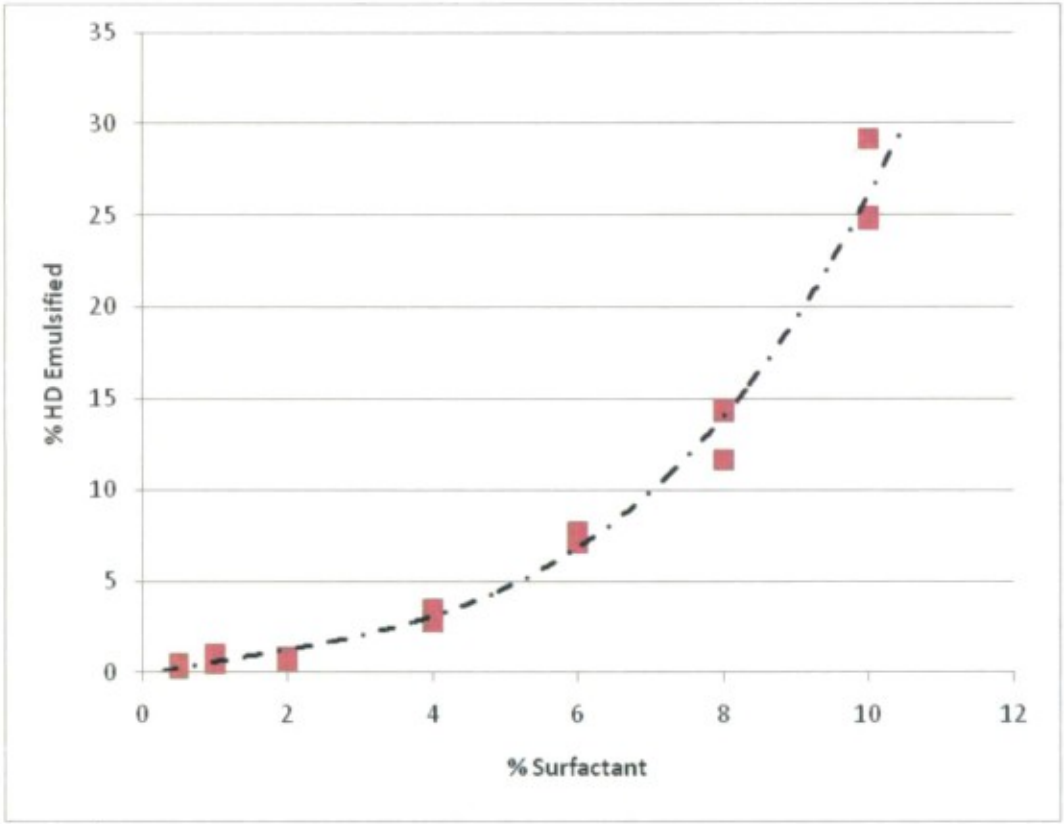


Figure 15. Emulsification of HD as a function of surfactant concentration following a long static period.

In conclusion, the emulsification of HD is dependent on the HLB value of the surfactant solution, with optimal performance observed in the 10 to 14 HLB range. The emulsification is also influenced by the specific surfactant system (i.e., Span/Tween or 15-S Tergitols) used to produce the HLB value surfactant system. The percent HD emulsified is also dependent on the surfactant concentration and the length of the static period following the emulsification process. Concentrations of surfactants surfactant (Tergitol 15-S-3 and Tergitol 15-S-40 at HLB 12) in the 6 to 10% range, provided about 85% emulsification of HD.

3.4 Surfactant Effect on GD and VX Reactions

Micelles generally increase the rates of bimolecular reactions of hydrophobic substrates and reactant anions by concentrating both reactants at the colloidal surface. This is where the high local concentrations result in a faster bimolecular reaction than in the bulk aqueous phase.

The surfactant effect on percarbonate reactions with VX and GD was studied. Reactions were performed in aqueous solutions containing 0, 1, 2, and 5% cetyltrimethyl-ammonium bromide (CTAB) surfactant. The CTAB surfactant concentrations were higher than the critical micelle concentration, which is 9.2×10^{-4} M in pure water at 25 °C.[15]

The kinetics of VX and GD neutralization by percarbonate was investigated in aqueous cationic micellar media at 21° C, at pH 10 and 9, respectively. The results are shown in Table 25 and Figure 16 for VX, and in Table 26 and Figure 17 for GD.

Table 25. VX neutralization by percarbonate as a function of surfactant concentration.

Time (s)	CTAB (%)	ln[VX]			
		Rep 1	Rep 2	Rep 3	Average
60	0	-5.617	-5.589	-5.546	-5.584
300		-6.331	-6.192	-6.156	-6.226
600		-6.903	-6.933	-6.89	-6.909
900		-7.616	-7.624	-7.528	-7.589
1200		-8.212	-8.289	-8.198	-8.233
60	1	-5.478	-5.508	-5.54	-5.509
300		-5.933	-5.991	-5.967	-5.964
600		-6.443	-6.459	-6.552	-6.485
900		-6.889	-6.946	-6.995	-6.943
1200		-7.427	-7.352	-7.436	-7.405
60	2	-5.484	-5.396	-5.425	-5.435
300		-5.824	-5.704	-5.723	-5.750
600		-6.31	-6.174	-6.144	-6.209
900		-6.675	-6.552	-6.535	-6.587
1200		-7.056	-6.856	-6.814	-6.909
60	5	-5.347	-5.402	-5.326	-5.358
300		-5.569	-5.613	-5.606	-5.596
600		-5.886	-5.976	-5.909	-5.924
900		-6.256	-6.289	-6.324	-6.290
1200		-6.535	-6.655	-6.655	-6.615

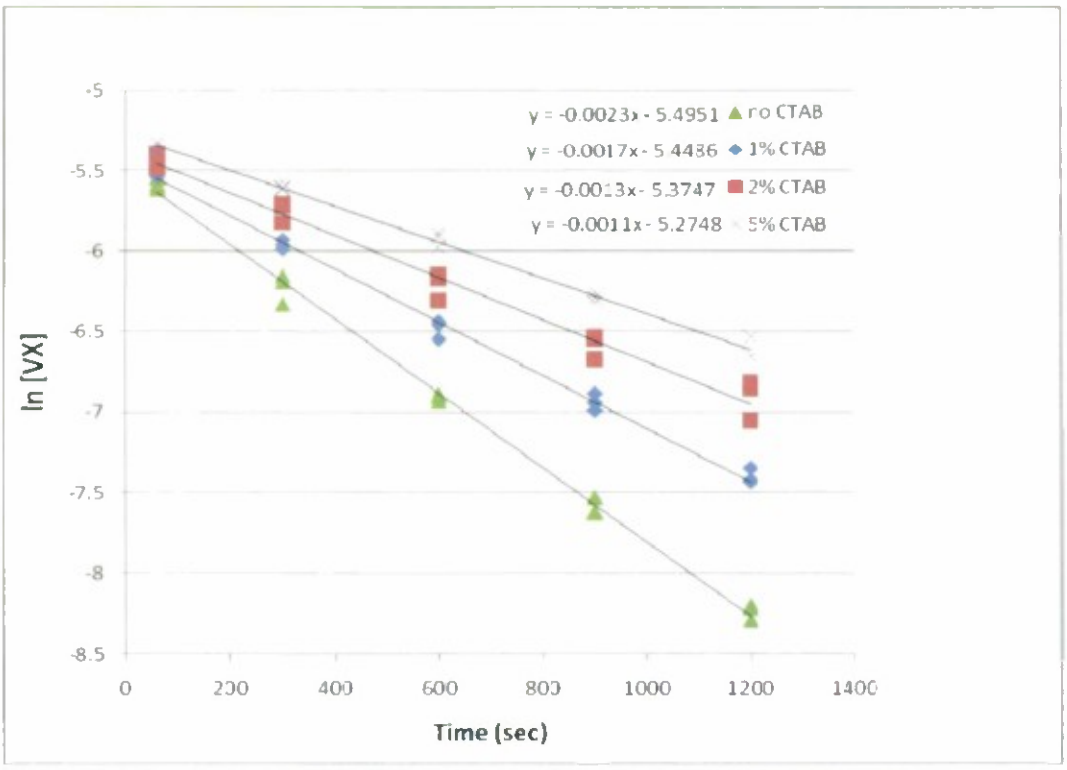


Figure 16. VX neutralization by percarbonate as a function of surfactant concentration.

Table 26. GD neutralization by percarbonate as a function of surfactant concentration.

Time (s)	CTAB (%)	ln[GD]			
		Rep 1	Rep 2	Rep 3	Average
60	0	-8.793	-8.799	-8.795	-8.796
300		-9.248	-9.263	-9.302	-9.271
600		-9.818	-9.792	-9.828	-9.813
900		-10.253	-10.364	-10.307	-10.308
1200		-10.783	-10.836	-10.726	-10.782
60	1	-8.833	-8.924	-8.879	-8.879
300		-9.519	-9.588	-9.513	-9.540
600		-9.952	-9.977	-10.022	-9.983
900		-10.466	-10.638	-10.565	-10.557
1200		-10.872	-10.980	-10.856	-10.903
60	2	-8.876	-8.769	-8.780	-8.808
300		-9.325	-9.210	-9.341	-9.292
600		-9.814	-9.707	-9.712	-9.744
900		-10.122	-10.089	-10.135	-10.115
1200		-10.551	-10.315	-10.501	-10.456
60	5	-8.706	-8.741	-8.936	-8.794
300		-9.196	-9.276	-9.369	-9.280
600		-9.658	-9.713	-9.737	-9.703
900		-10.202	-10.193	-10.165	-10.187
1200		-10.538	-10.578	-10.564	-10.560

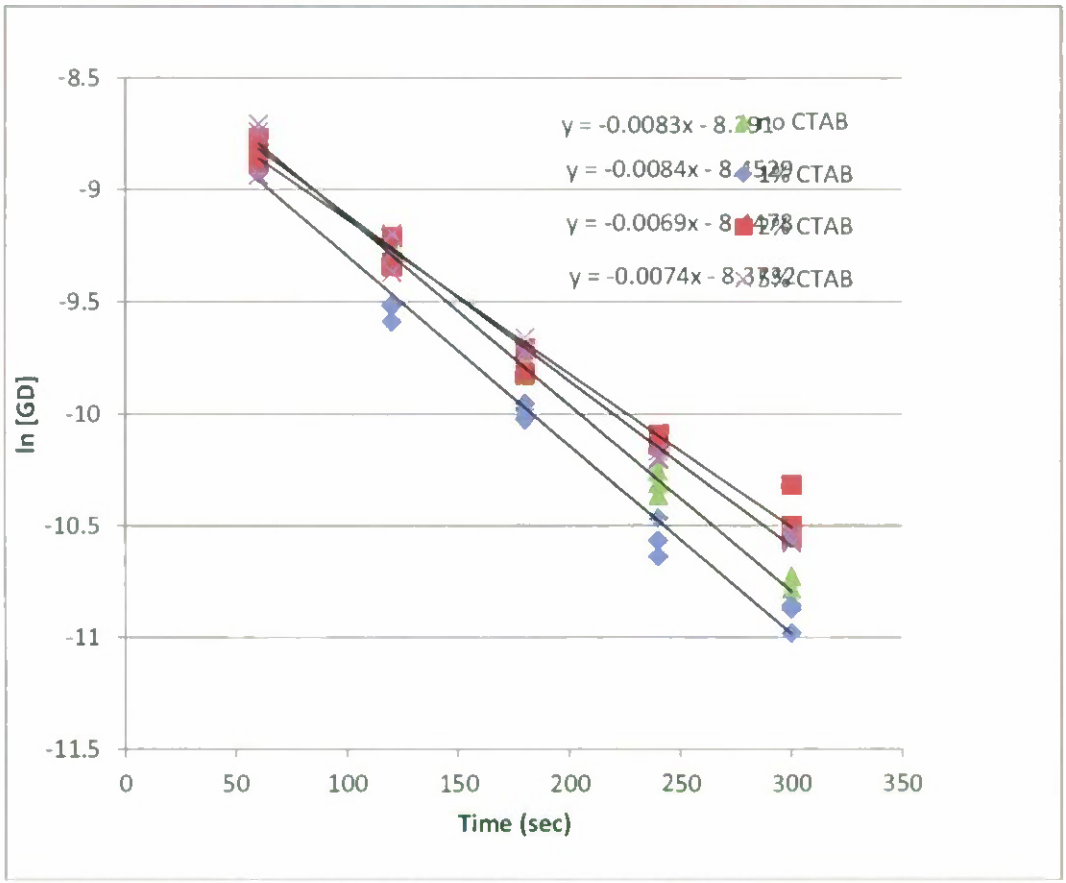


Figure 17. GD neutralization by percarbonate as a function of surfactant concentration.

Rate-surfactant profiles for reactions in solutions of CTAB were not typical of bimolecular micellar-assisted reactions. Little or no rate enhancement was observed in either the VX or the GD reactions. Rates were typically depressed slightly, with deviations being less than one order of magnitude relative to background with no CTAB.

The pseudo-first-order rate constant for VX neutralization decreased with increasing concentration of CTAB. As shown in Table 25 and Figure 16, at 5 wt % CTAB, the observed VX reaction rate was depressed by 50%, relative to reactions with no CTAB.

The effect of CTAB concentration on the neutralization rate of GD by percarbonate, at pH 9 was also assessed. As shown in Table 26 and Figure 17, the observed GD reaction rate showed no effect in the presence of 1% CTAB, but decreased slightly with increasing concentration of CTAB. At 2 wt % CTAB, the GD neutralization rate was depressed by 17%, relative to reactions with no surfactant.

The addition of CTAB to aqueous solutions of GD and VX did not provide rate enhancement, possibly because the substrates were too hydrophilic to promote micelle formation. Under these conditions, the rates in solutions with CTAB addition would resemble the rates from the bulk aqueous phase (without CTAB).

3.5 Solvent Polarity Effect on VX and GD Reactions

Solvents are frequently formulated into aqueous decontamination solutions to boost agent solubility, to depress the freezing point, or to provide increased penetration into contaminated surfaces. Water is highly polar, therefore, the addition of a less polar organic cosolvent effectively reduces the solution polarity, with a concomitant reduction in the reaction rate for nucleophilic reactions by anionic reactive species.

The effect of solvent polarity on the observed reaction rate of agents VX and GD was studied in solutions of peroxoborate, peracetic acid, and peroxomonosulfate (Oxone). Polarity of the reaction media was varied using aqueous solutions containing 0, 10, 20, and 30% propylene glycol. Propylene glycol is a non-flammable, relatively non-toxic antifreeze solvent, with the potential to be used in decontamination formulations. Because of these traits, it was selected to decrease the polarity of the aqueous reaction media, which was used to assess the effect of polarity on the observed reaction rate of agents. Using the dielectric strength as a measure of solution polarity, the polarity of the reaction solutions was varied by mixing water and propylene glycol in various proportions by volume.

As the solutions become less polar they are less able to solvate salts. The lower range of the dielectric constant was limited by the ability of the water/propylene glycol solutions to completely solvate the buffer salts used to maintain constant pH. The volume fraction of propylene glycol in the solutions was, therefore, limited to an upper value of 0.3, and the buffer strength was maintained at 0.1M to allow complete dissolution of the salts.

The observed and relative rate constants, related to the dielectric constant of the solution are presented in Table 27 and Table 28, respectively.

Table 27. Solvent polarity effect on observed rate constant.

Dielectric constant	Observed Rate Constant (k_{obs}, s^{-1})			
	0.025mM GD + 0.5mM Peroxoborate, pH 10	0.005M VX + 0.1M Oxone, pH 1.9	0.005M VX + 0.1M PAA, pH 9	0.005M VX + 0.1M Peroxoborate, pH 10
80.10	-0.0063	-0.00449	-0.0255	-0.000538
75.29	-0.0057	-0.00342	-0.0217	-0.000410
70.48	-0.0033	-0.00274	-0.0365	-0.000400
65.67	-0.0016	-0.00225	-0.0326	-0.000410

PAA = peracetic acid

Table 28. Solvent polarity effect on relative reaction rate.

Dielectric constant	Relative Reaction Rate (% of rate in water)			
	0.025mM GD + 0.5mM Peroxoborate, pH 10	0.005M VX + 0.1M Oxone, pH 1.9	0.005M VX + 0.1M PAA, pH 9	0.005M VX + 0.1M Peroxoborate, pH 10
80.10	100.0	100.0	100.0	100.0
75.29	90.5	76.2	85.1	76.2
70.48	52.4	61.0	143.1	74.3
65.67	25.4	50.1	127.8	76.2

PAA = peracetic acid

There was a general decrease in the observed reaction rates as the solvent polarity decreased, as shown in Table 27 and Table 28. The observed Oxone reaction rate with VX decreased as the solvent polarity decreased. In the least polar solutions, prepared using 30% propylene glycol, the observed VX reaction rate was depressed by 50% relative to reactions with higher polarity where no propylene glycol was added. Similar, but more pronounced behavior was seen in the GD reaction with peroxoborate where the observed reaction rate was depressed by 75%. The observed peroxoborate reaction rate with VX was depressed by 25% in solutions containing 10% propylene glycol, but the rate was similarly depressed in solutions containing higher concentrations of propylene glycol. The observed reaction rate of peracetic acid with VX was initially depressed by the addition of 10% solvent, but was unexpectedly enhanced in less polar solutions containing 20 and 30% solvent.

The observed decreases in the reaction rates of VX and GD, with decreasing solvent polarity (associated with increased solvent addition), are attributed primarily to a decrease in the degree of dissociation of the neutral oxidants to the active anionic species in the less polar media.[16] Additionally, the decrease in oxidation rate of VX by anionic oxidants as the polarity of the solvent decreases, may also be attributed to the N+-O− ion-pair complexes in the transition state.[17]

4. CONCLUSIONS

The influence of solution pH on the reaction rate of VX with peracetic acid, peroxoborate, peracetylborate, peroxomonocarbonate, and percarbonate was studied. The use of peracetic acid, peracetylborate, and peroxomonocarbonate/hydrogen peroxide solutions provided the highest reactivity with VX in the low alkaline range (pH 8–9). During testing, percarbonate and peroxoborate were reactive with VX, but reacted the least in the pH 8–10 range relative to the other oxidant solutions. With the exception of peracetic acid and peracetylborate, all of the oxidants tested resulted in greater reactivity in aqueous solutions as the pH increased. Peracetic acid resulted in the highest VX reaction rate, with an optimal VX reactivity at pH 9, while the use of peracetylborate resulted in an optimal rate in solutions at pH 8. Although peracetylborate is a source of peracetic acid, the differences revealed in the observed rate constants between the peracetylborate and the peracetic acid solutions may be because of the availability of peracetic acid provided in the peracetylborate solution. The observed background reaction rate of VX in the absence of a reactive oxidant was very low, and was an insignificant contribution relative to the observed reactivity of VX in the presence of a reactive constituent.

The influence of surfactant type on spore removal was also studied. Aqueous solutions containing 0.01 wt % surfactants, in addition to water without surfactant, were evaluated for spore removal efficacy as a function of surfactant type from CARC, rubber, and glass surfaces. Surfactants (Tween 80, SDS, and CTAB), representing each surfactant type (non-ionic, anionic, and cationic, respectively), provided similar rankings for spore removal irrespective of surface type. Using the anionic surfactant, SDS, provided the best spore removal from all the surfaces.

The relationship between the surfactant HLB number and its ability to emulsify HD was studied using two different surfactant systems, a Span/Tween system and a 15-S Tergitol system. The use of Tergitol solutions, with HLB values in the 10 to 14 range, provided the maximum emulsification of HD. Using solutions in this range resulted in approximately 60% emulsification of the HD. Emulsification provided by the Tergitol surfactant blends decreased sharply at HLB values above or below this range. Testing with Span/Tween solutions provided a resulted in a range of HLB values, providing maximum emulsification of HD compared with the Tergitol solutions. Using solutions with HLB values ranging from 6 to 14 provided results with approximately 60% emulsification of the HD. The emulsification provided by using the Span/Tween surfactant blends decreased sharply at HLB values below this range, but fairly good HD emulsification was retained at values up to 17.

Emulsion experiments, conducted to determine the concentration of HD emulsified as a function of the surfactant concentration, showed that in Tergitol 15-S solutions, with an HLB value of 12, the percent HD emulsified after sitting static for a period of 1 min increased logarithmically. The percent HD leveled off to a maximum value of about 85% in aqueous solutions containing 6 to 10 wt % surfactant. The HD emulsified after a much longer static period of 4 h increased exponentially as the surfactant concentration was increased. Solutions containing 10% surfactant emulsified 25% of the HD. In contrast to the HD emulsification in a short static period, increases in the surfactant concentration resulted in a greater increase in HD emulsification with a long static period as the surfactant concentration increased from 4 to 10%.

The effect of solvent polarity on the observed reaction rate of agents VX and GD was studied in solutions of peroxoborate, peracetic acid, and peroxomonosulfate (Oxone). Polarity of the reaction media was varied using aqueous solutions containing 0, 10, 20, and 30% propylene glycol. The observed Oxone reaction rate with VX decreased as the solvent polarity decreased. In the least polar solutions, prepared using 30% propylene glycol, the observed VX reaction rate was depressed by 50% relative to reactions with higher polarity where no propylene glycol was added. Similar, but more pronounced behavior was seen in the GD reaction with peroxoborate, where the observed reaction rate was depressed by 75%. The observed peroxoborate reaction rate with VX was depressed by 25% in solutions containing 10% propylene glycol, but the rate was similarly depressed in solutions containing higher concentrations of propylene glycol. The observed reaction rate of peracetic acid with VX was initially depressed by the addition of 10% solvent, but was unexpectedly enhanced in less polar solutions containing 20 and 30% solvent.

The observed decreases in reaction rates of VX and GD with decreasing solvent polarity are attributed primarily to a decrease in the degree of dissociation of the neutral oxidants to the active anionic species in the less polar media.[16] Additionally, the decrease in oxidation rate of VX by anionic oxidants as the polarity of the solvent decreases may also be attributed to the N+-O− ion-pair complexes in the transition state.[17]

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